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Cu(I) Networks With Polycyanoaromatic Ligands

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Cu(I) Networks with Polycyanoaromatic Ligands

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in Department of Chemistry from The College of William and Mary

by

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Cu(I) Networks with Polycyanoaromatic Ligands

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Abstract

The copper(I) complex \([\text{Cu(NCMe)}_4]\text{BF}_4\) was reacted with several cyanoaromatic ligands to form metal-organic oligomers and polymers. The ligands used included 1,2-dicyanobenzene (oDCB), 1,3-dicyanobenzene (mDCB), 1,4-dicyanobenzene (pDCB), 4,5-dicyanoimidazole (DCI), 2,3-pyrazinedicarbonitrile (2,3DCB), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 3-cyanopyridine (mCPy). Five novel crystal structures were solved: dimeric \([\text{Cu}_2(\text{PPh}_3)_4(oDCB)]_2(\text{BF}_4)_2\) and \([\text{Cu}_2(\text{PPh}_3)_4{oDCB}]_2(\text{BF}_4)_2\cdot0.5\text{CH}_2\text{Cl}_2\), polymeric \([\text{Cu}_2(\text{PPh}_3)_4(mDCB)]_n(\text{BF}_4)_2\) and \([\text{Cu}_2(\text{PPh}_3)_4(pDCB)]_2(\text{BF}_4)_2\cdot\text{CH}_2\text{Cl}_2]_n\), and trimeric \([\text{Cu}_3(\text{PPh}_3)_6(mCPy)]_3(\text{BF}_4)_3\). The potential of \([\text{Cu}_2(\text{PPh}_3)_4(oDCB)]_2(\text{BF}_4)_2\) as a chemical sensor for volatile organic compounds (VOCs) has been tested through film casting. Exposure to acetone, ethyl sulfide and ether produced no change to the emission of the films. Also, exposure to acetonitrile, morpholine and tetrahydrothiophene quenched the fluorescence. However, exposure of the remaining films to VOCs resulted in emission wavelengths in the blue-green and yellow-orange ranges.
Introduction

Metal-organic frameworks

Metal-organic frameworks (MOFs) are extended network structures in which metal centers are connected to form chains, sheets, or lattices by polydentate organic ligands. The variety of metal centers, oxidation states, coordination geometries, organic linker ligands and structural motifs offers an almost infinite number of possible combinations. A further aspect associated with MOFs is that they can be created with different dimensionalities, such as zero-dimensional molecules, one-dimensional chains, two-dimensional sheets, or three-dimensional networks, the latter of which can, in some cases, be porous in nature. Because the choice of metal centers and linker ligands will lead to different stoichiometries, dimensionalities, and/or structures, judicious choice of both metal atoms and organic linkers is crucial for the design of functional MOFs. Copper(I) cyanide is a good example of a one-dimensional (1D) chain. It is a very unusual inorganic salt because most inorganic salts form 2D or 3D structures. Its 2-coordinate metal atoms and lack of inter-chain bonding produce an infinite – Cu-C≡N-Cu-C≡N- chain structure. Two phases of CuCN are known. At low temperatures, the chain structure is wavy. However, in the high-temperature phase, the CuCN chain structure is strictly linear and all chains are parallel to one another. Graphene (although not a metal-organic network) is a monolayer of carbon atoms arranged in a 2D honeycomb structure. Figure 1 presents an
overview of the different MOF dimensionality.

**Figure 1.** The combination of metal atom and linker leads to different dimensionality structures.

In many cases a single set of components can be used to produce many networks having different stoichiometries, networking behavior, and dimensionality.

Various characteristics of MOFs make them potentially useful in many applications. Heterogeneous catalysis of gas-phase and solution reactions was one of the earliest proposed applications for MOFs. In such applications, MOFs would compete with a class of porous aluminosilicate minerals called zeolites. A common feature of zeolites and MOFs is uniform porosity. This porosity leads to large internal surface areas, which facilitate catalytic reactivity. As purely inorganic materials, zeolites are extraordinarily robust and often work well under extreme conditions. However, MOFs can be synthesized in a much greater
variety. The internal surface area and structure of the MOFs can potentially be rationally controlled with proper choice of organic ligands.

Gas storage is another potentially important application of MOFs. The surface area of MOFs is usually very high, and in some cases one gram of MOF’s surface area could cover up to forty tennis courts. This incredibly large surface area is the main reason for the large gas storage capacity. Because of the large MOF surface area, gas molecules can easily adsorb onto the surface. An adsorbed molecule is no longer able to freely diffuse as a gas. This means that a tank filled with MOF material can store more gas than an empty tank of equal volume. Some MOFs can bear high temperatures, making them potentially great materials for gas separation.\(^1\) The pore size of a MOF can be controlled to facilitate the efficient capture of particular-sized hydrocarbon molecules during petroleum refining. The porosity and large surface areas associated with MOFs also suggests to other applications such as molecule sensing and magnetic materials.\(^6\)

Most of the applications noted above take advantage of the ability of porous 3-D MOFs to act as hosts for small guest molecules. However, because of the entropy-based tendency to preclude empty space, porous networks are often formed either with solvent molecules filling the vacancies, or as multiple identical networks that are nested so as to fill one another's vacancies. In some cases, removal of the entrained solvent causes the MOF network to collapse, as indicated via X-ray analysis. The thermal stability of MOFs varies greatly, in some case limiting their use as sorbents for small molecules.\(^2\)
Copper(I)

Generally speaking, d<sup>10</sup> transition metals are good candidates for the construction of photoluminescent materials because electrons from the full d-subshell are often easily excited into s- or p-orbitals, or into vacant ligand orbitals (a process referred to as metal to ligand charge transfer – MLCT). Thus the d<sup>10</sup> electronic configuration results in several forms of luminescent behavior.<sup>5</sup> Particular attention has been paid to the photochemical and photophysical properties of Cu(I) complexes. Recently, highly fluorescent red copper nanoclusters have been investigated for involvement in synergistic anticancer activity.<sup>10</sup> However, it is difficult to detect copper(I) species by normal spectroscopic methods such as visible absorption because the copper(I) ion lacks d → d transitions.<sup>9</sup> The electron configuration of Cu(I) is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> (see Figure 2). As a d<sup>10</sup> metal, Cu(I) lacks coordination geometry preferences due to its lack of crystal field stabilization. The most common geometries for Cu(I) are 4-coordinate (tetrahedral), 3-coordinate (trigonal planar), and 2-coordinate (linear).

![Figure 2: Electronic Configuration of Cu(I)](image-url)
Figure 2. Electron configuration of Cu(I) in a tetrahedral crystal field.

Nitrile ligands

A nitrile is any organic compound that has a -C≡N function group. The term “cyano-” can be used interchangeably with nitrile. Cyano-organic ligands have been studied because of their diverse structures, as well as potential catalytic and magnetic properties. When organic nitrile ligands are used to synthesize transition metal complexes, the nitrogen atom has the ability to behave both as a σ-donor and π-acceptor ligand. Behaving as σ-donor and π-acceptor means when coordinated it forms one σ bond (single bond) and a weak π interaction with the metal center. The σ-donor property is relatively weak because the cyano group is relatively electron-withdrawing. π-Acceptance is also relatively weak in RCN. Thus, organo-nitriles are expected to be relatively weak ligands, and therefore exhibit significant lability. Figure 3 shows the σ-donor property of the -C≡N function group. Figure 4 shows the π-acceptor nature of the -C≡N function group, as well as the origin of metal to ligand charge transfer (MLCT), which serves as the source of photophysical excitation in many d^{10} complexes. If the metal is in a low oxidation state (electron rich) and the ligand possesses π-accepting properties (e.g., for CO or CN⁻) then an MLCT transition may occur. Moving electron density from the metal d-subshell to empty π-antibonding orbital enhances metal–ligand π-bonding.
Examples of RCN complexes with transition metals

Hard-soft acid-base (HSAB) theory provides evidence to help in understanding the stability of Cu(I) and RCN complexes. All transition metals are Lewis acid and all ligands are Lewis bases. Hardness and softness depends on the relative charge diffuseness of the metal or ligands. This charge diffuseness is related to oxidation state and effective nuclear charge of the metals and of the ligands.\textsuperscript{4} Since Cu(I) has a relatively low cationic charge, it is regarded as a relatively soft acid. Because of its diffuse $\pi$ electron cloud, nitriles are rather soft bases. Thus, according to HSAB theory, reaction between Cu(I) and RCN is greatly favored under equilibrium. Although nitrile ligands are quite common, they are easily replaced. This is why acetonitrile complexes of transition metals (see \textbf{Figure 5}) are routinely used as synthetic starting materials.
**Figure 5.** Known monomeric first row transition metal organonitrile complexes.

**Figure 5.** shows the known structures of first row transition metal complexes bond with RCN ligands. In $[\text{M}($RCN$)_6][\text{A}]_2$ complexes, the metal center is almost perfectly octahedrally surrounded by six nitrile ligands. However, Cu(I) ligated by four nitrile molecules and shows a slightly distorted tetrahedral structure. Another Cu(II) complex $[\text{Cu}($MeCN$)_2][\text{B(C}_6\text{F}_5)_4]$ is linearly coordinated.\textsuperscript{14}
Volatile organic compounds

Volatile organic compounds (VOCs) are a class of solids or liquids that emit vapor at room temperature. While human beings can smell most VOCs, other VOCs have no odor. Odor does not necessarily indicate the level of risk from inhalation. There are a great many VOCs to which we are exposed in our daily life. Some common examples include: acetone, benzene, ethylene glycol, formaldehyde, toluene and so on. VOCs are found both indoors and outdoors. Various household products such as building materials (paints, vinyl floors), home and personal care products (air fresheners) and various activities in daily life (cooking, smoking) lead to exposure to VOCs. Studies have shown that the level of VOCs indoors is generally two to five times higher than the level of VOCs outdoors.

Exposure to VOCs puts human beings’ health at risk. Common exposure to VOCs is divided into two categories: short-term exposure and long-term exposure. Short-term exposure to VOCs may lead to eye, nose/throat irritation, headaches, etc. On the other hand, long-term exposure leads to more serious problems such as cancer and liver damage. Because of these harmful effects associated with VOCs, their detection and reduction is desirable. Thus, there is an on-going need for sensitive and selective detection of vapor-phase analytes in daily life, including industrial process management, chemical threat detection, medical diagnostic, food quality control, occupation safety and environmental monitoring.
Recently, several investigators have also begun exploring the potential of MOFs as chemical sensors for VOCs and other classes of harmful compounds. The many advantages of MOF structures and properties stand out from other classes of chemosensory materials. The effectiveness of chemical sensors depends upon several factors: sensitivity, selectivity, response time, stability and reusability. Development of MOFs as sensing materials necessitates satisfied most of these requirements. With respect to designing a functional framework as a sensor material, proper choice of the organic linker is crucial and in this respect several aliphatic and aromatic polycaboxylates have been extensively used for synthesis of different of MOF different dimensionalities. Highly porous MOFs should be more sensitive and selective for vapor detection because they can more easily capture analyte molecules. However, substrate molecules can potentially become too well-entrained within more porous networks and thus decrease the sensitivity of the material. As a result 1D metallopolymers might work better as sensor materials in some cases. CuCN is a proven example for 1D MOFs as a sensor material. As mentioned above, CuCN is an unusual inorganic salt which forms an infinite chain structure. In MOF terms, CuCN is a 1D metallopolymers with coordinative vacancies at each metal center. Analyte molecules can adsorb to and be released from these Cu(I) centers more readily because the metal centers are more exposed. In this case, the sensitivity of 1D CuCN chain structure could prove to be superior to that of porous networks.

Chemical sensors and sensor systems for VOC detection
Chemical sensors are devices or instruments that determine the detectable presence, concentration, or quality of a given analyte. Chemical sensors are classified into seven categories according to Adam Hulanicke’s paper published in 1991. The seven types of sensors according to Hulanicke are: *Optical, Electrochemical, Electrical, Mass sensitive, Magnetic, Thermometric and Other.*

Electrochemical sensors convert effect of electrochemical interactions into a useful signal, e.g., in voltammetric sensors. In electrical sensors no electrochemical process takes place, but rather the signal arises from the change in electrical properties due to an interaction of the sensor with analyte. This is the case with electrolytic conductivity sensors. A mass sensitive sensor undergoes a mass change on the surface of the sensor when a signal is being detected. When magnetic sensors are exposed to a gas, a change of paramagnetic properties occurs. Thermometric sensors function by measuring the heat effects of a specific chemical reaction that occurs when the sensor is exposed to analyte. Other sensor such as X-ray sensors may use for determining the chemical composition of materials. In this thesis, I will mainly focus on *Optical sensors.* Optical sensor signals are optical phenomena such as luminescence, absorbance or reflectance are caused by the interaction of analyte and receptor part. The phenomenon may also be persistent or transitory.
Figure 6. Basic schematic of a sensor system (The lower flow chart outlines the steps of sensor system considered in the present research)

Figure 6 shows a flow chart outlining the general mechanism of a sensor system. The three major aspects of a sensor system are the analyte, transduction platform and signal processing.

Luminescence spectroscopy and detection

Luminescence describes the emission of light by a substance not resulting from the input of heat. Chemical reaction, electrical energy, subatomic motion, or stress on a crystal can cause luminescence. According to a Jablonski diagram (Figure 7), when targeted molecules are exposed to a light source of appropriate wavelength, each molecule absorbs a photon, following route A in the diagram. This promotes the electronic structure of the molecule from the ground state to an excited electronic state. The internal conversion that follows absorption and precedes emission is the result of energy loss through vibrational relaxation.

Photoemission is collectively referred to as luminescence (or photoluminescence). There are two varieties of luminescence: fluorescence and
phosphorescence. Fluorescence is one pathway for the emission of light by a substance that has absorbed light or other electromagnetic radiation. Fluorescence occurs when an electron of a molecule relaxes to its ground state by emitting a photon of light after route A without a change in spin state. Electronic states of molecules fall into two broad categories, singlet states and triplet states. A singlet state is one in which all of the electrons in the molecule have their spins paired. A triplet state is one in which one of the electrons in the molecule is unpaired.

Phosphorescence, unlike fluorescence, does not immediately result in the re-emission of the energy absorbed. This is because there is a change from singlet to triplet spin state that must occur before the molecule relaxes to its ground state. The intersystem crossing needed to convert a single state species to a triplet state species is quantum mechanically forbidden. Therefore, these transitions occur very slowly in certain materials. As a result, the phenomenon of phosphorescence may occur over a period from microseconds up to hours after the original excitation.

Figure 7. Jablonski diagram.
Luminescent materials are used for sensing in various areas, including chemical, physical and biological applications. In general, luminescent materials have detection advantages such as long lifetimes (in the case of phosphorescence), high brightness and large sensitivities (when the efficiency of light re-emission is high). Most luminescent materials are excitable in the UV or violet wavelength range. Light emitting diodes (LEDs) are used as light sources in detector systems because of their nearly monochromatic spectral characteristics and compactness.

Very recently, the luminescence properties of MOFs have become an active topic for investigation, since they have potential applications in chemical sensors, photochemistry, and electroluminescent displays. In addition, through judicious selection of ligands and metal atoms and the photophysics of MOFs should be tunable, allowing the desired luminescence behavior to be achieved.

The formation of photoemissive adducts to MOFs could potentially used as a basis for a sensing strategy for the detection of VOCs in the air. As shown in Figure 8, optimally, the MOF should remain non-emissive under UV exposure, and become emissive only after exposure to a VOC. UV light would thus serve as a tool to visualize the detector response. In order for this detection system to work, the MOF substrate should be castable as a film. Also, MOFs should have rapid, sensitive, and reversible response to VOCs in order to be useful sensors. Quick detector response is crucial because dangerous VOCs must be rapidly identified in order to reduce harm. High sensor sensitivity is also required when
detecting VOCs that are harmful even at low concentrations. Sensor reversibility is of importance since low cost and environmental friendliness are important economic considerations.

**Figure 8.** Sensing strategy for detection of VOCs.

In the research described herein we set out to discover the potential of various polycyanoaromatic ligands as luminescent indicators. It was hoped that the relative lability of nitrile groups in bridging ligands would enable the reversible changes in luminescence behavior that would provide the foundation for detection of nucleophilic VOCs. Nevertheless, release of one end of a polydentate ligand should not lead to complete decomposition of the detector complex. In the work described below [Cu(NCMe)₄]⁺ was reacted with various bridging cyanoaromatic ligands to produce metal-organic complexes. The crystal structures of each photoluminescent product was determined, and the film-casting and VOC response of one complex was studied.

**Experimental**

**Materials and methods**

All reagents were purchased from Aldrich or Acros and used without purification,
except for the complex $[\text{Cu(NCMe)}_4]\text{BF}_4$ which was prepared using a modified literature method.

**Synthesis of $[\text{Cu}_2(\text{PPh}_3)_4(B)]_2\text{BF}_4$ Complexes ($B =$ Bridging Ligand)**

$[\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2$

*Method A:* $[\text{Cu(NCMe)}_4]\text{BF}_4$ (0.157 g, 5.00 mmol) was dissolved in 15 mL of CH$_2$Cl$_2$. Then PPh$_3$ (0.264 g, 10.00 mmol) and oDCB (0.064 g, 5.00 mmol) were gradually added within one minute. The mixture was stirred at room temp. overnight. A clear tan solution appeared and was evaporated down to about 7 mL under vacuum, and then precipitated with addition of excess ether. The suspension was cooled for 15 min in the refrigerator. A white precipitate formed and was collected via vacuum filtration and washed with ether. The yellow product, $[\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2$, was dried under vacuum overnight. (0.305 g, 1.89 mmol, 75.96%)

*Method B:* $[\text{Cu(NCMe)}_4]\text{BF}_4$ (0.160 g, 5.00 mmol), PPh$_3$ (0.265 g, 10.00 mmol) and oDCB (0.065 g, 5.00 mmol) were mixed together with 20 mL of CHCl$_3$. The suspension was heated and stirred on a hot plate at 60 Celsius for 1 h. A white precipitate formed and was collected via vacuum filtration and washed with ether. The yellow product, $[\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2$, was dried under vacuum overnight (0.383 g, 2.38 mmol, 95.2%).

*Method C:* $[\text{Cu(NCMe)}_4]\text{BF}_4$ (0.157 g, 5.00 mmol), PPh$_3$ (0.265 g, 10.00 mmol) and oDCB (0.065 g, 5.00 mmol) were mixed together in 20 mL of CHCl$_3$. The mixture was heated and stirred on a hot plate until all CHCl$_3$ was evaporated. Ether was added
to the dark sticky oily product, which was then ultra-sonicated. The product was too sticky and could not be collected. This method failed to produce a tractable

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(oDCB)}_2\text{](BF}_4\text{)}_2 \text{] product.} \]

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(mDCB)}_2\text{](BF}_4\text{)}_2 \]

**Method A:** The compound was prepared in an analogous fashion to

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(oDCB)}_2\text{](BF}_4\text{)}_2, \text{ using [Cu(NCMe)}_4\text{]BF}_4 \text{ (0.158 g, 5.00 mmol), PPh}_3 \text{ (0.264 g, 10.00 mmol) and mDCB (0.064 g, 5.00 mmol), yielding 0.352 g of the white product (2.19 mmol, 87.6%).} \]

**Method C:** The compound was prepared in an analogous fashion to

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(oDCB)}_2\text{](BF}_4\text{)}_2, \text{ using [Cu(NCMe)}_4\text{]BF}_4 \text{ (0.156 g, 5.00 mmol), PPh}_3 \text{ (0.264 g, 10.00 mmol) and mDCB (0.064 g, 5.00 mmol), yielding 0.39 g of the white product (2.43 mmol, 97.2%).} \]

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(pDCB)}_2\text{](BF}_4\text{)}_2 \]

**Method C:** The compound was prepared in an analogous fashion to

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(oDCB)}_2\text{](BF}_4\text{)}_2, \text{ using [Cu(NCMe)}_4\text{]BF}_4 \text{ (0.156 g, 5.00mmol), PPh}_3 \text{ (0.262 g, 10.00 mmol) and pDCB (0.066 g, 5.00 mmol), yielding 0.339 g of the yellow product (2.11 mmol, 84.4%).} \]

**Method D:** \[ \text{[Cu(NCMe)}_4\text{]BF}_4 \text{ (0.157 g, 5.00 mmol), PPh}_3 \text{ (0.267 g, 10.00 mmol) and pDCB (0.067 g, 5.00 mmol) were mixed together in 10 mL of CH}_2\text{Cl}_2. \text{ The solution was stirred at room temperature for 2 h. Then the solution was then poured into ether and within seconds the solution turned cloudy. The cloudy solution (25 mL) was} \]
placed into the freezer overnight. The neon yellow precipitate was collected next day via vacuum filtration and dried on a vacuum line overnight. (0.356 g, 2.22 mmol, 88.8%).

\[\text{Cu}_3(\text{PPh}_3)_6(\text{mCPy})_3(\text{BF}_4)_2\]

**Method C:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\), using \([\text{Cu} (\text{NCMe})_4]\text{BF}_4\) (0.157 g, 5.00 mmol), \text{PPh}_3\) (0.262 g, 10.00 mmol) and mCPy (0.052 g, 5.00 mmol), yielding 0.349 g of the yellow-green fluorescent product (3.95 mmol, 79.0%).

\[\text{Cu}_2(\text{PPh}_3)_4(\text{DCI})_2(\text{BF}_4)_2\]

**Method A:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\), using \([\text{Cu} (\text{NCMe})_4]\text{BF}_4\) (0.159 g, 5.00 mmol), \text{PPh}_3\) (0.263 g, 10.00 mmol) and DCI (0.059 g, 5.00 mmol), no precipitate formed after reducing the volume.

\[\text{Cu}_2(\text{PPh}_3)_4(2,3\text{PDC})_2(\text{BF}_4)_2\]

**Method A:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\), using \([\text{Cu} (\text{NCMe})_4]\text{BF}_4\) (0.158 g, 5.00 mmol), \text{PPh}_3\) (0.263 g, 10.00 mmol) and 2,3PDC (0.114 g, 5.00 mmol), yielding gold/grey precipitate (0.313 g, 1.94 mmol, 77.8%).

\[\text{Cu}_2(\text{PPh}_3)_4(\text{DDQ})_2(\text{BF}_4)_2\]

**Method A:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\), using \([\text{Cu} (\text{NCMe})_4]\text{BF}_4\) (0.158 g, 5.00 mmol), \text{PPh}_3\)
(0.262 g, 10.00 mmol) and DDQ (0.113 g, 5.00 mmol), yielding 0.318 g of the brown red product (1.98 mmol, 79.2%).

**Synthesis of \([\text{Cu}_2(\text{PPh}_3)_2(B)_2]\text{BF}_4\) Complexes**

\(\text{Cu}_2(\text{PPh}_3)_2(\text{oDCB})_2(\text{BF}_4)_2\)

**Method A:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2]\text{BF}_4_2\), using \([\text{Cu}(\text{NCMe})_4]\text{BF}_4\) (0.158 g, 5.00 mmol), \(\text{PPh}_3\) (0.131 g, 5.00 mmol) and oDCB (0.097 g, 7.50 mmol), yielding 0.033 g of a light yellow product (0.27 mmol, 10.8%).

**Method C:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2]\text{BF}_4_2\), using \([\text{Cu}(\text{NCMe})_4]\text{BF}_4\) (0.157 g, 5.00 mmol), \(\text{PPh}_3\) (0.133 g, 5.00 mmol) and oDCB (0.097 g, 7.50 mmol), yielding a sticky brown product which could not be collected.

\(\text{Cu}_2(\text{PPh}_3)_2(\text{mDCB})_2(\text{BF}_4)_2\)

**Method A:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2]\text{BF}_4_2\), using \([\text{Cu}(\text{NCMe})_4]\text{BF}_4\) (0.157 g, 5.00 mmol), \(\text{PPh}_3\) (0.133 g, 5.00 mmol) and mDCB (0.097 g, 7.50 mmol), yielding 0.19 g of a white milky product (1.57 mmol, 62.8%).

**Method C:** The compound was prepared in analogous fashion to \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2]\text{BF}_4_2\), using \([\text{Cu}(\text{NCMe})_4]\text{BF}_4\) (0.158 g, 5.00 mmol), \(\text{PPh}_3\) (0.132 g, 5.00 mmol) and oDCB (0.097 g, 7.50 mmol), yielding 0.288 g of a white product with cold blue luminescence (2.38 mmol, 95.2%).

\(\text{Cu}_2(\text{PPh}_3)_2(\text{pDCB})_2(\text{BF}_4)_2\)
Method D: [Cu(NCMe)$_4$]BF$_4$ (0.157 g, 5.00 mmol), PPh$_3$ (0.136 g, 5.00 mmol) and pDCB (0.097 g, 7.50 mmol) were mixed together in 10 mL of CH$_2$Cl$_2$. The mixture was stirred at room temp. for 2 h. After 2 h, ether was poured into the resulting solution and within seconds the solution turned into cloudy. The cloudy solution was placed into freezer overnight. The light blue precipitate was collected the next day via vacuum filtration and dried under vacuum overnight (0.198 g, 1.64 mmol, 65.6%).

Method C: The compound was prepared in analogous fashion to [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$, using [Cu(NCMe)$_4$]BF$_4$ (0.157 g, 5.00 mmol), PPh$_3$ (0.131 g, 5.00 mmol) and pDCB (0.099 g, 7.50 mmol), yielding 0.305 g of the blue product (2.52 mmol, 100%).

[Cu$_2$(PPh$_3$)$_2$(DCI)$_2$](BF$_4$)$_2$

Method A: The compound was prepared in analogous fashion to [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$, using [Cu(NCMe)$_4$]BF$_4$ (0.157 g, 5.00 mmol), PPh$_3$ (0.132 g, 5.00 mmol) and DCI (0.087 g, 7.50 mmol). A light green precipitate formed (0.095 g, 0.805 mmol, 32.2%).

[Cu$_2$(PPh$_3$)$_2$(2,3 PDC)$_3$](BF$_4$)$_2$

Method A: The compound was prepared in analogous fashion to [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$, using [Cu(NCMe)$_4$]BF$_4$ (0.158 g, 5.00 mmol), PPh$_3$ (0.131 g, 5.00 mmol) and 2,3PDC (0.171 g, 7.50 mmol), yielding a yellow-orange precipitate (0.093 g, 0.62 mmol, 24.8%).

[Cu$_2$(PPh$_3$)$_2$(DDQ)$_3$](BF$_4$)$_2$

Method A: The compound was prepared in analogous fashion to [Cu$_2$
(PPh₃)₄(oDCB)₂][BF₄]₂, using [Cu(NCMe)₄]BF₄ (0.159 g, 5.00 mmol), PPh₃ (0.133 g, 5.00 mmol) and DDQ (0.170 g, 7.50 mmol), yielding a pink-grey milky residue (0.269 g, 1.79 mmol, 71.6%).

**Synthesis of [Cu(B)₂][BF₄]**

[Cu(oDCB)₂][BF₄]

*Method A:* [Cu(NCMe)₄]BF₄ (0.157 g, 5.00 mmol) and oDCB (0.130 g, 10.1 mmol) were mixed together in 15 mL CH₂Cl₂. The solution was stirred under room temperature over night, yielding 0.143 g of the white product collected via vacuum filtration. (1.98 mmol, 79.2%).

[Cu(mDCB)₂][BF₄]

*Method A:* The compound was prepared in analogous fashion to [Cu(oDCB)₂][BF₄] using [Cu(NCMe)₄]BF₄ (0.158 g, 5.00 mmol) and mDCB (0.130 g, 10.1 mmol) yielding 0.166 g of a white product (2.3 mmol, 92%).

[Cu(DCl)₂][BF₄]

*Method A:* The compound was prepared in analogous fashion to [Cu(oDCB)₂][BF₄] using [Cu(NCMe)₄]BF₄ (0.163 g, 5.11 mmol) and DCI (0.118 g, 10.0 mmol) yielding 0.173 g of the white product (1.89 mmol, 75.6%).

**Film casting**

Casting of [Cu₂(PPh₃)₄(oDCB)₂][BF₄]₂ films: All films were cast onto microscope cover glasses that were pre-cleaned by dipping in concentrated nitric acid, rinsing with deionized water, and drying with acetone. 100 µL of a 100 mM
[\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) solution in \text{CH}_2\text{Cl}_2\) or \text{CHCl}_3\) were pipetted onto the pre-cleaned cover glasses. A doctor blade with a gap height of 0.635 mm was run across the solution on the glass slide, followed by the evaporation of the remaining solution by placing the slide on a heated glass surface at 32 °C for 5 min.

**Exposure of films to organic vapor**

A film was placed on a platform inside a 4 oz. glass jar. 3-4 drops of organic liquid was placed at the bottom of the jar, which was then sealed with a screw cap. The films were exposed for 30 min and then examined for luminescence emission under 365 nm black light.

**Crystal growth**

Crystals of both 2:4:2 and 2:2:3 ratio products for oDCB, mDCB and pDCB were grown in three solvent combinations: \text{CH}_3\text{NO}_2/ether, \text{CHCl}_3/ether, and \text{CH}_2\text{Cl}_2/ether. In each case a 20 mmol solution of the complex was prepared in \text{CH}_3\text{NO}_2, \text{CHCl}_3, or \text{CH}_2\text{Cl}_2. About 1 mL of the 20 mmol solution was placed in a 5 mm i.d. tube filling the tube to about 1/3 of its height. The remaining 2/3 of the tube was filled with ether, creating a layer interface between the solvents. The tubes were allowed to stand for several days to allow crystals to grow.

**X-Ray structure determinations**

Single crystal structural determinations were carried out using a Bruker SMART Apex II diffractometer using graphite-monochromated Cu Kα radiation. The data were corrected for Lorentz and polarization effects and absorption using SADABS. The structures were solved by use of direct methods or Patterson map. Least squared
refinement on $F^2$ was used for all reflections. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL package of software. The non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were located and then placed in theoretical positions.\textsuperscript{4}

**Results and discussion**

The object of this study was to evaluate the potential of Cu(I) complexes bridged with various cyanoaromatic ligands as luminescent indicators for VOCs. The relatively weak coordination of the RC≡N–Cu should enable partial ligand substitutions by nucleophilic VOCs without fully disrupting the network structure. It is hoped that nucleophile substitution for the nitrile ligand might result in changes in luminescence emission behavior. Using X-ray crystallography, I was attempting to get a crystal structure of each compound in order to further structural understanding of the networking behavior of the ligands studied. The products are to be exposed to various nucleophilic VOCs for the exploration of the photophysical properties of the novel complexes thereafter.

**Synthesis of copper(I) metal-organic complexes with bridging ligands**

The following ligands have been used in the current project: 1,2-dicyanobenzene (oDCB), 1,3-dicyanobenzene (mDCB), 1,4-dicyanobenzene (pDCB), 4,5-dicyanoimidazole (DCI), 2,3-pyrazinedicarbonitrile (23DCB),
2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 3-cyanopyridine (mCPy) (see Figure 9). These ligands react with [Cu(NCMe)$_2$(PPh$_3$)$_2$]$^+$ (itself produced in situ) to produce metal-organic framework complexes. Figure 10 presents the general reaction strategy used in the study.

**Figure 9.** Various ligands used in the study
Four methods were used to synthesize various Cu(I) complexes. Method A involved dissolving $[\text{Cu(NCMe)}_4]\text{BF}_4$ in dichloromethane followed by stoichiometric addition of triphenylphosphine ($\text{PPh}_3$, two equivalents) and cyanoaromatic ligand (one equivalent). After stirring overnight and concentrating under vacuum, the solution was precipitated by the addition of ether and cooling. Method B involved the mixing of the components in chloroform and heating on a hot plate with solvent evaporation until a precipitate was formed. Method C was similar to Method B, except that the solution was removed from the hot plate before the solvent was fully evaporated. Ether was then added and the resulting suspension was ultra-sonicated to precipitate the product. Method D was related to method A, but in this case, the $\text{CH}_2\text{Cl}_2$ solution was precipitated by addition of ether without cooling.

Method A was used to synthesize all complexes during the initial stage of the study. However, for pDCB, method A did not produce any precipitate. For this preparation, method C was created and tested with pDCB at first. It successfully yielded $[\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2](\text{BF}_4)_2$ as a bright yellow solid in good yield.
The success of the methods varied among the different complexes. **Table 1** presents the color and percent yield data for all the cyanoaromatic ligand products. For most of the products except \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\), method C was found to give the best results. However, \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) could not be synthesized through method C, and method B proved to be best in this case.

**Table 1.** Percent yield and color of various reaction products.

a) Ratio of \([\text{Cu}(\text{NCMe})_4]\text{BF}_4:\text{PPh}_3:\text{Cyanoaromatic} = 2:4:2\)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Product Color</th>
<th>Method A</th>
<th>Method B</th>
<th>Method C</th>
<th>Method D</th>
</tr>
</thead>
<tbody>
<tr>
<td>oDCB</td>
<td>Grey/white</td>
<td>76.0</td>
<td>95.2</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>mDCB</td>
<td>White</td>
<td>87.6</td>
<td>−</td>
<td>97.2</td>
<td>−</td>
</tr>
<tr>
<td>pDCB</td>
<td>Neon yellow</td>
<td>−</td>
<td>−</td>
<td>84.4</td>
<td>88.8</td>
</tr>
<tr>
<td>23DCP</td>
<td>Gold/grey</td>
<td>77.8</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>DCI</td>
<td>No product</td>
<td>0</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>DDQ</td>
<td>Brown red</td>
<td>79.2</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>mCPy</td>
<td>Green</td>
<td>−</td>
<td>−</td>
<td>79.0</td>
<td>−</td>
</tr>
</tbody>
</table>

b) Ratio of \([\text{Cu}(\text{NCMe})_4]\text{BF}_4:\text{PPh}_3:\text{Cyanoaromatic} = 2:2:3\)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Product Color</th>
<th>Method A</th>
<th>Method B</th>
<th>Method C</th>
<th>Method D</th>
</tr>
</thead>
<tbody>
<tr>
<td>oDCB</td>
<td>Light yellow</td>
<td>10.8%</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>mDCB</td>
<td>White milky</td>
<td>62.8%</td>
<td>−</td>
<td>95.2%</td>
<td>−</td>
</tr>
<tr>
<td>pDCB</td>
<td>Light blue</td>
<td>−</td>
<td>−</td>
<td>100%</td>
<td>65.6%</td>
</tr>
<tr>
<td>23DCP</td>
<td>Yellow/orange</td>
<td>32.2%</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Ligand</td>
<td>Color</td>
<td>Method A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oDCB</td>
<td>White</td>
<td>79.2%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mDCB</td>
<td>White</td>
<td>92.0%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCI</td>
<td>White</td>
<td>75.6%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 11** shows the predicted structures of products of the reactions run at [Cu(MeCN)$_4$]BF$_4$:PPh$_3$:Cyanoaromatic ratio of 2:4:2. Only the products formed from the DCB and mCPy ligands showed luminescence. Other 2:4:2 products were not studied further. Each 2:4:2 product was expected to have two copper metal centers each capped with two PPh$_3$ ligands and bridged by a dicyanoaromatic ligand. Figure 12 shows the predicted structures of products of the reactions run at a ratio of 2:2:3. Each of these compounds was expected to show two [(PPh$_3$)Cu]$^+$ centers linked to form a dimer by three bridging ligands. However, when prepared, these complexes showed no luminescence. Therefore, they were not further pursued.
Figure 11. Predicted structures of 2:4:2 products that showed luminescence.

Figure 12. Predicted structures of 2:2:3 products that showed no luminescence
Crystallographic Structures

**Structural description of \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\)**

The crystal structure of \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) solved in the monoclinic space group \(P2_1/c\). The X-ray structure showed a bridged \(\text{Cu}(\text{PPh}_3)_2^+\) dimer linked by \(\text{o-dicyanobenzene}\) ligands. Thus, a symmetrical dimer unit contained two copper(I) metal centers, two bridging \(\text{o-dicyanobenzene}\) ligands and four triphenylphosphine ligands. However, only one half of the molecule (one copper) was found to be crystallographically independent. The remaining half of the molecule was generated via an inversion center that lay in the center of the 14-member \(\text{Cu}_2(\text{oDCB})_2\) ring. The single unique \(\text{BF}_4^-\) ion showed fluorine disorder over two positions. This was modeled as two interpenetrating ions sharing a common boron center.

Each four-coordinate Cu(I) atom was bound to nitrogen atom of each oDCB and P donor atoms from two \(\text{PPh}_3\) ligands to generate a distorted tetrahedron. The bond angles for a regular tetrahedron are expected to be 109.5° when all four substituents exert the same steric influence. However, the angles of the Cu(I) tetrahedron in complex \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) ranged from 98.27° to 122.28°. The dihedral angles between P3-Cu2-P4 and P1-Cu1-P2 were 122.28° and 120.94°, respectively. These large angles between atoms were no doubt due to significant steric hindrance between intramolecular two \(\text{PPh}_3\) ligands. Another large angle deviation from the tetrahedral ideal was the N4-Cu2-P4 angle, which was only 98.27°. In the dinuclear core the Cu–Cu separation is 6.296 Å and the
Cu–Cu separations between two adjacent molecules were 12.724 Å and 15.156 Å.

The Cu-N bond lengths in the present dimer were 2.057 Å and 2.015 Å, while in the related complex [CuI(PPh3)(2,2-bipy)], the distances were 2.070 Å and 2.082 Å.\textsuperscript{12} The distances between Cu-P in the oDCB dimer were 2.270 Å and 2.257 Å, while in the related [CuI(PPh3)(DPPZ)]:DMF, the distance between Cu-P was 2.2146 Å. Figure 13 shows the structures of [CuI(PPh3)(DPPZ)]:DMF and [Cu2(PPh3)4(oDCB)2](BF4)2. The dipyridophenazine (DPPZ) ligand is essentially planar and is therefore is similar to oDCB ligand, which is also planar. Comparing these two distances to other observed tetrahedral Cu(I) complexes and PPh3, the distances between Cu-N and Cu-P were found to be basically the same. Table 2 and Table 3 present the crystal data for [Cu2(PPh3)4(oDCB)2](BF4)2. Figure 14 and Figure 15 show a bridged dimer unit and packing diagram of [Cu2(PPh3)4(oDCB)2](BF4)2.\textsuperscript{13}

![Figure 13](image)

**Figure 13.** The structures of [CuI(PPh3)(DPPZ)] (left) and [Cu2(PPh3)4(oDCB)2](BF4)2 (right).

**Table 2.** Crystal data for [Cu2(PPh3)4(oDCB)2](BF4)2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C88 H68 B2 Cu2 F8 N4 P4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1606.04</td>
</tr>
</tbody>
</table>
Temperature 100(2) K
Wavelength 1.54178 Å
Crystal system Monoclinic
Space group P2₁/c
Unit cell dimensions $a = 10.2544(4)$ Å $\alpha = 90^\circ$
$b = 21.8677(9)$ Å $\beta = 100.6235(15)^\circ$
$c = 17.5324(7)$ Å $\gamma = 90^\circ$
Volume 3864.1(3) Å³
$Z$ 2
Density (calculated) 1.380 Mg/m³
Absorption coefficient 2.028 mm⁻¹
$F(000)$ 1648
Crystal size 0.460 x 0.280 x 0.070 mm³
Theta range for data collection 3.265 to 66.998°
Index ranges $-12 \leq h \leq 12$, $-26 \leq k \leq 26$, $-20 \leq l \leq 20$
Reflections collected 44637
Independent reflections 6847 [R(int) = 0.0334]
Completeness to theta = 67.679° 98.0 %
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 6847 / 6 / 504
Goodness-of-fit on $F^2$ 1.079
Final R indices [I>2sigma(I)] $R1 = 0.0402$, $wR2 = 0.0985$
R indices (all data)  \[ R1 = 0.0412, \quad \text{wR2} = 0.0992 \]

Largest diff. peak and hole 1.005 and −0.473 e Å\(^{-3}\)

**Table 3.** Selected bond lengths [Å] and angles [°] for \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\).  

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(2)#1</td>
<td>2.003(2)</td>
<td>N(1)-C(1)</td>
<td>1.146(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.0472(19)</td>
<td>N(2)-C(8)</td>
<td>1.144(3)</td>
</tr>
<tr>
<td>Cu(1)-P(1)</td>
<td>2.2547(6)</td>
<td>N(2)-Cu(1)#1</td>
<td>2.003(2)</td>
</tr>
<tr>
<td>Cu(1)-P(2)</td>
<td>2.2717(6)</td>
<td>N(2)-Cu(1)#1</td>
<td>2.003(2)</td>
</tr>
<tr>
<td>P(1)-C(9)</td>
<td>1.827(2)</td>
<td>N(2)#1-Cu(1)-N(1)</td>
<td>105.01(8)</td>
</tr>
<tr>
<td>P(1)-C(15)</td>
<td>1.828(2)</td>
<td>N(2)#1-Cu(1)-P(1)</td>
<td>117.47(6)</td>
</tr>
<tr>
<td>P(1)-C(21)</td>
<td>1.830(2)</td>
<td>N(1)-Cu(1)-P(1)</td>
<td>108.27(6)</td>
</tr>
<tr>
<td>P(2)-C(27)</td>
<td>1.814(2)</td>
<td>N(2)#1-Cu(1)-P(2)</td>
<td>104.67(6)</td>
</tr>
<tr>
<td>P(2)-C(33)</td>
<td>1.822(2)</td>
<td>N(1)-Cu(1)-P(2)</td>
<td>97.71(5)</td>
</tr>
<tr>
<td>P(2)-C(39)</td>
<td>1.824(2)</td>
<td>P(1)-Cu(1)-P(2)</td>
<td>120.94(2)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1
**Figure 14.** The bridged dimer of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$. Color scheme for all X-ray structure diagrams: Orange = Cu, pale orange = P, blue = N, grey = C, pink = B, yellow-green = F. Copper and directly bonded atoms shown in ball-and-stick form; other atoms shown as wireframe. Hydrogen atoms omitted for clarity.

**Figure 15.** Two packing diagram views of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$. 

**Structural Description of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$**

A second crystalline form of the 2:4:2 oDCB complex was encountered. The crystal structure of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$ was very similar to that of the solvent-free structure of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$. Which structure was formed experimentally depended upon from what solvent system the crystals were grown. Crystals of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$ (described above) were grown from chloroform layered with ether. On the other hand, [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$ was grown from dichloromethane layered with ether. In this case a half molecule of CH$_2$Cl$_2$ per dimer unit was found in the structure. The dimer unit in this case was found to be fully crystallographically independent with two independent copper atoms that were not related by symmetry. The CH$_2$Cl$_2$ molecule showed crystallographic disorder which was modeled.

The crystal structure of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$ solved in the monoclinic $P2_1/c$ space group. Like the solvent-free complex, the X-ray structure showed a simple bridged dimer with two copper centers linked by two o-dicyanobenzene ligands. A symmetrical dimer unit contained two copper(I) centers, two bridging o-dicyanobenzene ligands, and four triphenylphosphine ligands.

**Table 6** lists all major bond lengths and angles of all structures in this thesis for comparison to one another. The angles of the Cu(I) tetrahedron in complex [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$ ranged from 96.39° to 126.25°. The
angles between P1-Cu1-P2 and P3-Cu2-P4 were 122.38° and 126.25°. These large angles between atoms were due to the steric hindrance between two intramolecular PPh₃ ligands. Another large angle difference in the structure was the N3-Cu1-P2 angle, which was only 96.39°. In the dinuclear core the Cu–Cu separation was 6.162 Å and the Cu–Cu separations between two adjacent molecules were 11.827 Å and 15.67 Å.

The distances between Cu-N here were 2.003 Å and 2.100 Å, while in [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂, the distances were 2.057 Å and 2.015 Å. For the distances between Cu-P were 2.253 Å and 2.264 Å, while in [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂, the distances were 2.270 Å and 2.257 Å. After comparing these two distances to other tetrahedral Cu(I) complexes and PPh₃, the distance between Cu-N and Cu-P were found to be fairly similar. However, it was significant that the Cu-N distances were more unequal in the solvate complex, suggesting weaker bridging between monomers to form the dimer.

Table 4 and Table 5 present the crystal data and structural data for [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂·0.5CH₂Cl₂. Figure 16 shows a bridged dimer of [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂·0.5CH₂Cl₂ and Figure 17 shows the packing diagram of this complex. Figure 18 shows an overlay of the dimers for both solvent free and solvent-included structures. The symmetric nature of the oDCB units in the solvent-free dimer (in red) resulting from inversion symmetry is apparent in the overlay. However, the solvent-bearing dimer (in green) lacks this symmetry.
<table>
<thead>
<tr>
<th><strong>Table 4. Crystal data and structural refinement for</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>[Cu₂(PPh₃)₄(oDCB)₂][BF₄]₂·0.5CH₂Cl₂.</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₈₈.₅₀ H₆₉ B₂ Cl Cu₂ F₈ N₄ P₄</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1648.₅₀</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>1.₅₄₁₇₈ Å</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P₂₁/c</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>a = 11.₆₇₆₃(₂) Å</td>
<td>α = 90°</td>
</tr>
<tr>
<td>b = 41.₈₈₂₁(₈) Å</td>
<td>β = 106.₉₃₉₅(₈)°</td>
</tr>
<tr>
<td>c = 17.₃₅₆₄(₃) Å</td>
<td>γ = 90°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>8₁₁₉.₅(₃) Å³</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Density (calculated)</strong></td>
<td>1.₃₄₉ Mg/m³</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>2.₂₄₀ mm⁻¹</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>3₃₈₀</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.₂₅₇ x 0.₂₁₂ x 0.₁₂₄ mm³</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>2.₁₁₀ to 5₈.₉₄₅°</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-₁₂≤h≤₁₂, -₄₅≤k≤₄₆, -₁₉≤l≤₁₉</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>8₇₈₂₂</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>1₁₆₁₈ [R(int) = 0.₀₄₇₂]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 6₇.₆₇₉°</strong></td>
<td>7₉.₁ %</td>
</tr>
</tbody>
</table>
Refinement method  
Full-matrix least-squares on $F^2$

Data / restraints / parameters  
11618 / 6 / 1028

Goodness-of-fit on $F^2$  
1.074

Final R indices [I>2sigma(I)]  
$R_1 = 0.0428$, $wR_2 = 0.1029$

R indices (all data)  
$R_1 = 0.0500$, $wR_2 = 0.1073$

Largest diff. peak and hole  
0.684 and -0.812 e Å$^{-3}$

Table 5. Bond lengths [Å] and angles [°] for $\text{[Cu}_2\text{(PPh}_3)_4\text{(oDCB)}_2\text{](BF}_4)_2\cdot0.5\text{CH}_2\text{Cl}_2$. 

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Bond</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.003(3)</td>
<td>N(1)-C(9)</td>
<td>1.137(4)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.100(3)</td>
<td>N(2)-C(16)</td>
<td>1.136(4)</td>
</tr>
<tr>
<td>Cu(1)-P(1)</td>
<td>2.2527(8)</td>
<td>N(1)-Cu(1)-N(3)</td>
<td>103.08(11)</td>
</tr>
<tr>
<td>Cu(1)-P(2)</td>
<td>2.2637(8)</td>
<td>N(1)-Cu(1)-P(1)</td>
<td>107.17(8)</td>
</tr>
<tr>
<td>P(1)-C(29)</td>
<td>1.819(3)</td>
<td>N(3)-Cu(1)-P(1)</td>
<td>109.30(8)</td>
</tr>
<tr>
<td>P(1)-C(17)</td>
<td>1.823(3)</td>
<td>N(1)-Cu(1)-P(2)</td>
<td>116.05(8)</td>
</tr>
<tr>
<td>P(1)-C(23)</td>
<td>1.826(3)</td>
<td>N(3)-Cu(1)-P(2)</td>
<td>96.39(7)</td>
</tr>
<tr>
<td>P(2)-C(41)</td>
<td>1.827(3)</td>
<td>P(1)-Cu(1)-P(2)</td>
<td>122.38(3)</td>
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<tr>
<td>P(2)-C(47)</td>
<td>1.827(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(2)-C(35)</td>
<td>1.827(3)</td>
<td></td>
<td></td>
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</tbody>
</table>
Table 6. Comparison of angles (°) and bond lengths (Å) of all products.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Cu-P</td>
<td>122.28</td>
<td>126.25</td>
<td>128.50</td>
<td>125.23</td>
<td>119.05</td>
</tr>
<tr>
<td>P-Cu-N</td>
<td>98.27</td>
<td>96.39</td>
<td>103.24</td>
<td>95.89</td>
<td>96.94</td>
</tr>
<tr>
<td>Cu-N</td>
<td>2.057, 2.015</td>
<td>2.003, 2.100</td>
<td>2.019, 2.037</td>
<td>2.007, 2.098</td>
<td>1.900, 1.932</td>
</tr>
<tr>
<td>Cu-P</td>
<td>2.270, 2.257</td>
<td>2.253, 2.264</td>
<td>2.260, 2.265</td>
<td>2.266, 2.288</td>
<td>2.275, 2.281</td>
</tr>
</tbody>
</table>

A = [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$, B = [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$, C = [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$(BF$_4$)$_2$]$_n$, D = [Cu$_2$(PPh$_3$)$_4$(pDCB)$_2$(BF$_4$)$_2$·CH$_2$Cl$_2$]$_n$, E = [Cu$_3$(PPh$_3$)$_6$(mCPy)$_3$](BF$_4$)$_3$.

Figure 16. The bridged dimer unit for [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5CH$_2$Cl$_2$. The disordered solvent molecule is visible at top.
Figure 17. The packing diagram for [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5$\text{CH}_2\text{Cl}_2$

Figure 18. Overlay of the [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$]$_{2+}$ dimer portion of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$ (red) and [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$·0.5$\text{CH}_2\text{Cl}_2$ (green). All hydrogens and PPh$_3$ phenyls omitted, along with anion and solvent molecules.
**Structural description of [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$(BF$_4$)$_n$]**

The crystal structure of [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$(BF$_4$)$_n$] solved in the orthorhombic space group $P2_12_12_1$. The crystallographically independent unit showed a monomer of [Cu(PPh$_3$)$_2$(mDCB)](BF$_4$). However, symmetry-based expansion results in its expansion to a polymer structure. When extending the monomer to polymer, the polymer showed a 1D coordination chain connected by bridging mDCB ligands. However, this 1D chain structure also stacks into a 3D network as a result of a T-shape $\pi$-stacking. A T-shape $\pi$-stacking interaction is a non-covalent attractive force between pairs of aromatic rings. The positive electrostatic potential on one ring is aligned with negative electrostatic potential on another ring to form the $\pi$-stack. The $\pi$-stacking interaction in the current network occurs between aromatic rings in the PPh$_3$ ligands. The $\pi$-stacking interaction was shown in Figure 21.

A single monomer unit contains one copper(I) metal, one m-dicyanobenzene and two PPh$_3$ ligands. The four-coordinated Cu(I) atom is bound to two nitrogen atoms from two separate mDCB ligands and two P atoms to generate a distorted tetrahedron. The bond angles of the Cu(I) tetrahedron in complex [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$(BF$_4$)$_n$]$_n$ ranged from 103.24° for N-Cu-N to 128.50° for P1-Cu1-P2.

The nearest Cu–Cu distance within an mDCB polymer is 10.523 Å, while the nearest Cu–Cu separation between polymer strands is 12.557 Å. The Cu–Cu separations in [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$(BF$_4$)$_2$ complexes (without and with solvent)
were 6.296 Å, the 4.227 Å. The difference is the result of angular constraints associated with oDCB vs. mDCB and the resulting oligomeric structures. However, comparison to the Cu–Cu separation between adjacent layers showed only a 0.167 Å difference since the distance between Cu atoms in adjacent 
[Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$]$^+$ dimers complex was 12.724 Å. This tiny difference is negligible, and thus the packing of dimers vs. that of chains in these two complexes can be seen as closely related. **Table 6 lists all major bond lengths and angles of all structures in this thesis for comparison to one another.**

The distances between Cu-N in the mDCB polymer units were 2.019 Å and 2.037 Å, while in [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$, the distances were 2.057 Å and 2.015 Å. Also, for the distance between Cu-P in the mDCB units were 2.260 Å and 2.265 Å, while in [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$](BF$_4$)$_2$, the distance was 2.270 Å and 2.257 Å. Comparing these two distances with other observed tetrahedral Cu(I) complexes and PPh$_3$, the distances between Cu-N and Cu-P revealed little difference. **Table 7 and Table 8 presented the crystal data for** [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$](BF$_4$)$_2$]$_n$. **Figure 19 shows a monomer unit of** [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$](BF$_4$)$_2$]$_n$ and **Figure 20 shows a zigzag chain structure of this complex.**

**Table 7. Crystal data of [Cu$_2$(PPh$_3$)$_4$(mDCB)$_2$](BF$_4$)$_2$]$_n$.**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{44}$H$</em>{34}$B Cu F$_4$N$_2$ P$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>803.02</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
</tbody>
</table>
Wavelength 1.54178 Å

Crystal system Orthorhombic

Space group \( \text{P2}_1\text{2}_1\text{2}_1 \)

Unit cell dimensions
\[
\begin{align*}
a &= 14.7185(3) \text{ Å} & \alpha &= 90^\circ \\
b &= 15.7165(4) \text{ Å} & \beta &= 90^\circ \\
c &= 16.5877(4) \text{ Å} & \gamma &= 90^\circ \\
\end{align*}
\]

Volume 3837.12(16) Å\(^3\)

\( Z \)
4

Density (calculated) 1.390 Mg/m\(^3\)

Absorption coefficient 2.042 mm\(^{-1}\)

\( F(000) \)
1648

Crystal size 0.496 x 0.145 x 0.140 mm\(^3\)

Theta range for data collection 3.874 to 66.998°

Index ranges \(-17\leq h\leq 17, -18\leq k\leq 18, -16\leq l\leq 18\)

Reflections collected 45425

Independent reflections 6632 \([R(\text{int}) = 0.0323]\)

Completeness to theta = 67.679° 96.3%

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 6632 / 0 / 487

Goodness-of-fit on \( F^2 \) 1.048

Final R indices \([I>2\sigma(I)]\) \( R1 = 0.0199, \) \( wR2 = 0.0512 \)

R indices (all data) \( R1 = 0.0203, \) \( wR2 = 0.0515 \)
Absolute structure parameter -0.005(4)

Extinction coefficient n/a

Largest diff. peak and hole 0.181 and -0.351 e Å⁻³

**Table 8. Bond lengths [Å] and angles [°] for [Cu₂(PPh₃)₄(mDCB)₂(BF₄)]ₙ.**

<table>
<thead>
<tr>
<th>Bond Description</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(2)#1</td>
<td>2.0185(18)</td>
<td>N(1)-C(1) 1.139(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.037(2)</td>
<td>N(2)-C(8) 1.141(3)</td>
</tr>
<tr>
<td>Cu(1)-P(1)</td>
<td>2.2598(6)</td>
<td>N(2)-Cu(1)#2 2.0184(18)</td>
</tr>
<tr>
<td>Cu(1)-P(2)</td>
<td>2.2653(6)</td>
<td>N(2)#1-Cu(1)-N(1) 100.32(8)</td>
</tr>
<tr>
<td>P(1)-C(9)</td>
<td>1.821(2)</td>
<td>N(2)#1-Cu(1)-P(1) 112.36(6)</td>
</tr>
<tr>
<td>P(1)-C(15)</td>
<td>1.828(2)</td>
<td>N(1)-Cu(1)-P(1) 103.24(6)</td>
</tr>
<tr>
<td>P(1)-C(21)</td>
<td>1.831(2)</td>
<td>N(2)#1-Cu(1)-P(2) 104.46(6)</td>
</tr>
<tr>
<td>P(2)-C(27)</td>
<td>1.822(2)</td>
<td>N(1)-Cu(1)-P(2) 104.16(6)</td>
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<td>P(2)-C(33)</td>
<td>1.830(2)</td>
<td>P(1)-Cu(1)-P(2) 128.50(2)</td>
</tr>
<tr>
<td>P(2)-C(39)</td>
<td>1.831(2)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y,z+1/2    #2 -x+1/2,-y,z-1/2
Figure 19. A monomer unit of $[\text{Cu}_2(\text{PPh}_3)_4(m\text{DCB})_2(\text{BF}_4)]_n$.

Figure 20. Chain structure of $[\text{Cu}_2(\text{PPh}_3)_4(m\text{DCB})_2(\text{BF}_4)]_n$.

Figure 21. T-shape $\pi$-stacking interaction between aromatic rings in $[\text{Cu}_2(\text{PPh}_3)_4(m\text{DCB})_2(\text{BF}_4)]_n$. 
**Structural description of \([\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2(\text{BF}_4)\cdot\text{CH}_2\text{Cl}_2]_n\)**

The crystal structure of \([\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2(\text{BF}_4)\cdot\text{CH}_2\text{Cl}_2]_n\) solved in the monoclinic space group \(P2_1/c\). Crystallographic analysis showed the repeat unit to be \([\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2(\text{BF}_4)]\cdot\text{CH}_2\text{Cl}_2\). Each crystallographic repeat unit consisted of two monomers, which were parts of two separate polymer chains, two \(\text{BF}_4^-\) anions and two \(\text{CH}_2\text{Cl}_2\) molecules. Symmetry-based expansion results in monomer expansion to a polymer structure. The resulting zigzag polymer showed a 1D coordination chain connected by bridging pDCB ligands. This 1D chain structure forms a helix containing T-shape \(\pi\)-stacking interactions. The \(\pi\)-stacking interaction is shown in Figure 24. Both \(\text{CH}_2\text{Cl}_2\) molecules and one \(\text{BF}_4^-\) anion were disordered over two positions in the structure. In this case, the two \(\text{BF}_4^-\) positions did not share a common boron atom.

The bond angles of the Cu(I) tetrahedron in complex \([\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2(\text{BF}_4)\cdot\text{CH}_2\text{Cl}_2]_n\) range from 95.89° for N-Cu-N to 125.23° for P1-Cu1-P2. The nearest Cu–Cu distance within a pDCB polymer was 11.785 Å, while the nearest Cu–Cu separation between polymer strands was 8.760 Å. The distances between Cu–N in the pDCB polymer units were 2.007 Å and 2.098 Å. Also for the distances between Cu–P in the pDCB units were 2.266 Å and 2.288 Å. **Table 9** and **Table 10** present the crystal data and structural parameters for \([\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2(\text{BF}_4)\cdot\text{CH}_2\text{Cl}_2]_n\). **Figure 22** shows a monomer unit of \([\text{Cu}_2(\text{PPh}_3)_4(\text{pDCB})_2(\text{BF}_4)\cdot\text{CH}_2\text{Cl}_2]_n\) and **Figure 23** shows the zigzag chain structure of this complex. **Table 14** shows the comparison of zigzag chain angles.
between the mDCB and pDCB polymers. Angles in the mDCB polymer chain are probably larger because the zigzag chain lies in a single plane. In contrast, the pDCB polymer has smaller angles probably because it forms a helical shape.

**Table 9.** Crystal data and structure refinement for 

\[ \text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(pDCB)}_2\text{(BF}_4\text{-CH}_2\text{Cl}_2)]_n \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C45 H36 B Cl2 Cu F4 N2 P2</td>
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<tr>
<td>Formula weight</td>
<td>887.95</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>( a = 12.3905(3) ) Å</td>
<td>( \alpha = 90^\circ )</td>
</tr>
<tr>
<td>( b = 49.5897(12) ) Å</td>
<td>( \beta = 96.8549(14)^\circ )</td>
</tr>
<tr>
<td>( c = 13.7956(3) ) Å</td>
<td>( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>8416.0(3) Å</td>
</tr>
<tr>
<td>( Z )</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.402 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.057 mm(^{-1})</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>3632</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.289 x 0.207 x 0.123 mm(^3)</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.782 to 68.307°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14(\leq h \leq 14), -56(\leq k \leq 55), -15(\leq l \leq 16)</td>
</tr>
</tbody>
</table>
Reflections collected \hspace{1cm} 97628

Independent reflections \hspace{1cm} 14535 [R(int) = 0.0708]

Completeness to theta = 67.679° \hspace{1cm} 94.5 %

Refinement method \hspace{1cm} Full-matrix least-squares on F²

Data / restraints / parameters \hspace{1cm} 14535 / 0 / 1100

Goodness-of-fit on F² \hspace{1cm} 1.080

Final R indices [I>sigma(I)] \hspace{1cm} R1 = 0.0595, wR2 = 0.1378

R indices (all data) \hspace{1cm} R1 = 0.0708, wR2 = 0.1440

Largest diff. peak and hole \hspace{1cm} 0.693 and -0.657 e Å⁻³

Table 10. Selected Bond lengths [Å] and angles [°] for

\[ \text{[Cu}_2\text{(PPh}_3)_4(pDCB)_2\text{(BF}_4)_2\text{CH}_2\text{Cl}_2 \text{]}_n \]
Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1,-x+1,z    #2 -y+1,x-y,z    #3 -x+y,-x+1,z

#4 -y+1,x-y+1,z

Figure 22. A monomer unit of $\text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(pDCB)}_2\text{(BF}_4\text{)}\cdot\text{CH}_2\text{Cl}_2]_n$.  

Figure 23. Helix- chain coordination for $\text{[Cu}_2\text{(PPh}_3\text{)}_4\text{(pDCB)}_2\text{(BF}_4\text{)}\cdot\text{CH}_2\text{Cl}_2]_n$.  

56
Figure 24. T-shape π-stacking interaction between aromatic rings in [Cu$_2$(PPh$_3$)$_4$(pDCB)$_2$(BF$_4$)·CH$_2$Cl$_2$]$_n$.

**Structural description of [Cu$_3$(PPh$_3$)$_6$(mCPy)$_3$](BF$_4$)$_3$**

The crystal structure of [Cu$_3$(PPh$_3$)$_6$(mCPy)$_3$](BF$_4$)$_3$ solved in the trigonal space group $R3c$. The X-ray structure showed a trimeric unit [Cu$_3$(PPh$_3$)$_6$(mCPy)$_3$](BF$_4$)$_3$. This product was formed using a different ligand meta-cyanopyridine. The single unit of this crystal structure was a closed 18-member ring formed by three mCPy ligands bridging three Cu atoms. The crystallographic repeat unit represented a third of the trimer with a single copper(I) atom, one mCPy ligand and two PPh$_3$ ligands. Each four-coordinate Cu(I) atom was bound to one nitrogen atom in the pyridine of mCPy, one nitrogen in the cyano group of mCPy and two P donor atoms from PPh$_3$ to generate a distorted tetrahedron. Unusual positional disorder was seen in the mCPy ligand. As shown in Figure 25, C-C bonds representing a portion of the pyridine ring and its connection to cyano carbon were shared between the two ligand positions.
Figure 25. mCPy disorder in $[\text{Cu}_3(\text{PPh}_3)_6(\text{mCPy})_3]_3(\text{BF}_4)_3$

The angles of the Cu(I) tetrahedron in complex $[\text{Cu}_3(\text{PPh}_3)_6(\text{mCPy})_3]_3(\text{BF}_4)_3$ ranged from 96.94° to 119.05°. The dihedral angle of P1-Cu1-P2 was relatively modest: 119.05°. Another large angle difference for the trimer was found for the N2A-Cu1-N1A angle, which is only 96.94°. This was due to the internal angle constraint of the trimer structure. The P-Cu-N angles were difficult to evaluate because of the disorder in the mPCy ligand. For each P atom large and small P-Cu-N angles of about 97° and 115° are seen.

In the trinuclear core the Cu–Cu separation was 8.607 Å and the Cu–Cu separation with two adjacent trimers was 18.677 Å. For comparison, the layer separation of $[\text{Cu}_2(\text{PPh}_3)_4(\text{mDCB})_2(\text{BF}_4)]_n$ is 12.557 Å, the separation within $[\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2$ complex was 6.296 Å. Thus, the separation between $[[\text{Cu}_3(\text{PPh}_3)_6(\text{mCPy})_3]_3(\text{BF}_4)_3$ units seemed fairly large. The large steric hindrance of this structure might be affecting this distance.

The distances between Cu1-N2A (Nitrogen on the pyridine) were 2.214 Å and Cu1-N1A (Nitrogen in the cyano group) was 1.932 Å. Comparing to bond
lengths in the other cyano groups, the distance were basically the same. However, the bond length of Cu-N when the nitrogen in pyridine was significantly shorter than any of the cyano Cu-N distances measured. This was perfectly reasonable given the stronger bonding recognized for metal pyridine complexes over metal nitrile complexes. Comparing different Cu-P bond lengths with other observed tetrahedral Cu(I) complexes and PPh₃, the distance Cu-P was basically the same as well. **Table 11** and **Table 12** presented a basic crystal data of [Cu₃(Cu₃(PPh₃)₆(mCPy)₃)]₃(BF₄)₃. **Figure 26** and **Figure 27** show both a monomer structure and packing diagram of [Cu₃(PPh₃)₆(mCPy)₃](BF₄)₃.

**Table 11.** Crystal data of [Cu₃(PPh₃)₆(mDCB)₃](BF₄)₃

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₈₄ H₆₈ B₂ Cu₂ F₈ N₄ P₄</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1558.00</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>1.54178 Å</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Trigonal</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>R3c</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td>a = 23.0603(6) Å  α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 23.0603(6) Å  β = 90°</td>
</tr>
<tr>
<td></td>
<td>c = 36.0481(10) Å  γ = 120°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>16601.3(10) Å³</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>9</td>
</tr>
</tbody>
</table>
Density (calculated) 1.403 Mg/m$^3$
Absorption coefficient 2.104 mm$^{-1}$
F(000) 7200
Crystal size 0.49 x 0.31 x 0.11 mm$^3$
Theta range for data collection 3.303 to 66.978°
Index ranges -27<=h<=27, -20<=k<=27, -43<=l<=43
Reflections collected 22864
Independent reflections 6162 [R(int) = 0.0342]
Completeness to theta = 67.679° 98.6 %
Absorption correction Numerical
Max. and min. transmission 0.7483 and 0.3774
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 6162 / 1 / 488
Goodness-of-fit on F$^2$ 1.083
Final R indices [I>2sigma(I)] R1 = 0.0564, wR2 = 0.1426
R indices (all data) R1 = 0.0577, wR2 = 0.1438
Absolute structure parameter 0.80(6)
Largest diff. peak and hole 0.798 and -0.800 e Å$^{-3}$
Figure 26. A single unit of the [Cu₃(PPh₃)₆(mCPy)₃]₃(BF₄)₃. Disorder in mCPy is omitted.

Table 12. Bond lengths [Å] and angles [°] for [Cu₃(PPh₃)₆(mCPy)₃](BF₄)₃

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(1B)#1</td>
<td>1.900(19)</td>
<td>P(2)-C(37)</td>
</tr>
<tr>
<td>Cu(1)-N(1A)</td>
<td>1.932(9)</td>
<td>P(2)-C(31)</td>
</tr>
<tr>
<td>Cu(1)-P(2)</td>
<td>2.275(2)</td>
<td>N(1B)#1-Cu(1)-P(2)</td>
</tr>
<tr>
<td>Cu(1)-P(1)</td>
<td>2.281(3)</td>
<td>N(1A)-Cu(1)-P(2)</td>
</tr>
<tr>
<td>Cu(1)-N(2B)</td>
<td>2.40(2)</td>
<td>N(1B)#1-Cu(1)-P(1)</td>
</tr>
<tr>
<td>P(1)-C(19)</td>
<td>1.810(10)</td>
<td>N(1A)-Cu(1)-P(1)</td>
</tr>
<tr>
<td>P(1)-C(7)</td>
<td>1.818(10)</td>
<td>P(2)-Cu(1)-P(1)</td>
</tr>
<tr>
<td>P(1)-C(13)</td>
<td>1.835(8)</td>
<td>N(1B)#1-Cu(1)-N(2B)</td>
</tr>
<tr>
<td>P(2)-C(25)</td>
<td>1.832(9)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
Figure 27. Packing diagrams for [Cu₃(PPh₃)₆(mCPy)₃]₃(BF₄)₃. The upper view is along the a-axis and the lower view is along the c-axis. mCPy disorder is apparent in this latter view.

Table 13. Comparison of zigzag chain structure angles (°) in mDCB and pDCB

<table>
<thead>
<tr>
<th>Complex</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu₂(PPh₃)₄(mDCB)₂(BF₄)]ₙ</td>
<td>100.37, 103.64</td>
</tr>
<tr>
<td>[Cu₂(PPh₃)₄(pDCB)₂(BF₄)·CH₂Cl₂]ₙ</td>
<td>80.27, 73.59</td>
</tr>
</tbody>
</table>
Preparation of Cyanoaromatic Copper Complex Films

Two solvents dichloromethane and chloroform were used to prepare solutions for film casting. Films were formed by evaporation of these 100 mM solutions on glass microscope cover slides.

Film casting of \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) was carried out in order to determine the ability of metal complex as a VOC sensor. One desired characteristic of the film is a consistent and uniform surface. Two methods of film casting, evaporation and doctor-blade casting, were attempted during the study. In the evaporation casting method, \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) solution was micropipetted onto a clean glass cover slip and allowed to evaporate. However, the solution was too concentrated at one spot on the glass cover slip. When all solvent evaporated, some neon yellow color crystals appeared on one area of the glass slip. This method was considered unsuccessful because the film being cast did not have a consistent and uniform surface. On the other hand, the temperature for the evaporation may have been too low since the slide was not heated, resulting in crystalline films. In the doctor blade method of casting, \([\text{Cu}_2(\text{PPh}_3)_4(\text{oDCB})_2](\text{BF}_4)_2\) solution was micropipetted into a clean glass cover slip, the doctor blade was pulled over the solution, and then the solution was allowed to evaporate. The results of this method were also unsatisfactory because the doctor blade was not adjusted to the proper height. When the height was adjusted over 0.635 mm, the solution did not cover the whole surface uniformly. On the contrary, when the height was less than 0.635 mm, the doctor
blade swept away the solution from the glass slip as the doctor blade was moved across. Since these two film casting results did not yield satisfactory results, a new method for film casting was introduced. The clean glass cover slip was put on a preheated glass surface (35 °C). Then, the \([\text{Cu}_2(\text{PPh}_3)_4(o\text{DCB})_2](\text{BF}_4)_2\) solution was micropipetted onto a clean glass cover slip, a razor blade was used to pull over the solution, and the solution was allowed to evaporate on the heated glass surface. This method cast a fairly uniform and consistent film compare to the other methods. The films were slightly neon yellow colored and showed strong neon yellow fluorescence under exposure to 365 nm black light.

Results for film exposure to VOCs

Volatile organic compounds being used during the experiment were: acetonitrile, acetone, pyridine, 3-picoline, quinoline, piperidine, morpholine, tetrahydrofuran, ethyl sulfide, tetrahydrothiophene and diethyl ether.

The films were exposed to the saturated vapor pressure of various VOCs at ambient temperature. After the exposure, the luminescence of these films excited by 365 nm light was determined. The results are shown in Table 15. A diverse variety of phenomena were found, depending on the VOC used. There was not much difference in the results between dichloromethane and chloroform solvent used when casting. Unexposed \([\text{Cu}_2(\text{PPh}_3)_4(o\text{DCB})_2](\text{BF}_4)_2\) has an emission wavelength of ~570 nm, which gave a neon yellow color.

In the CH$_2$Cl$_2$ films, exposure to acetone, ethyl sulfide and ether produced no change to the emission of the films. However, exposure to acetonitrile, 3-picoline,
quinolone, morpholine and tetrahydrothiophene quenched the fluorescence. Exposure of the rest of the films to VOCs resulted in the emission wavelengths in the blue-green and yellow-orange ranges.

For chloroform films, exposure to acetone, quinolone, ethyl sulfide, tetrahydrofuran and ether yielded no change to the emission of the films. However, exposure to acetonitrile, piperidine, morpholine and tetrahydrothiophene turned the fluorescence off. The rest VOCs altered the emission wavelengths from neon yellow to blue-green and yellow-orange ranges. Table 14 and Figure 28 present results for exposure of [Cu$_2$(PPh$_3$)$_4$(oDCB)$_2$]$(BF_4)_2$ to various VOCs.

**Table 14.** Result for exposure to various VOCs

<table>
<thead>
<tr>
<th>VOC</th>
<th>Film cast from CH$_2$Cl$_2$</th>
<th>Film cast from CHCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>No luminescence</td>
<td>No luminescence</td>
</tr>
<tr>
<td>Acetone</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Luminescence decrease</td>
<td>Change to blue green luminescence</td>
</tr>
<tr>
<td>3-Picolene</td>
<td>No luminescence</td>
<td>Luminescence decrease</td>
</tr>
<tr>
<td>Quinoline</td>
<td>No luminescence</td>
<td>No change</td>
</tr>
<tr>
<td>Piperidine</td>
<td>Dark green solution onto the film</td>
<td>No luminescence</td>
</tr>
<tr>
<td>Morpholine</td>
<td>No luminescence</td>
<td>No luminescence</td>
</tr>
<tr>
<td>Compound</td>
<td>Change to blue green</td>
<td>No change</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>luminescence</td>
<td></td>
</tr>
<tr>
<td>Ethyl Sulfide</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Tetrahydrothiopene</td>
<td>No luminescence</td>
<td>No luminescence</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>No change</td>
<td>No change</td>
</tr>
</tbody>
</table>

a) Upper photos show original films without exposure to VOCs.

   Lower photos show films exposure to acetonitrile.
b) Upper photos show films exposure to acetone.

  Lower photos show films exposure to pyridine.


c) Upper photos show films exposure to 3-picoline.
Lower photos show films exposure to quinoline.

d) Upper photos show films exposure to piperidine

Lower photos show films exposure to morpholine.

e) Upper photos show films exposure to tetrahydrofuran.
Lower photos show films exposure to ethyl sulfide.

f) Upper photos show films exposure to tetrahydrothiophene.

Lower photos show films exposure to ether.

**Figure 28.** [Cu$_2$(PPh$_3$)$_4$($o$DCB)$_2$](BF$_4$)$_2$ after exposed to VOCs. The left two pictures were from CH$_2$Cl$_2$-cast films, the right two photos were CHCl$_3$-cast films.

**Conclusion**

Novel Cu(I) metal-organic complexes were created and tested as potential chemical sensors being a luminescence indicator for volatile organic compounds. In summary, several self-assembled metal-organic complexes of copper(I) and bridging polycyanoaromatic ligands (o-dicyanobenzene, m-dicyanobenzene,
p-dicyanobenzene, and m-cyanopyridine) have been successfully synthesized and characterized. Luminescence is found in complexes synthesized with a Cu(I):PPh₃:bridge ratio of 2:4:2. However, complexes synthesized with 2:2:3 and 2:0:1 ratios did not show luminescence. Since no luminescence was detected with these complexes, they were not studied further.

Five novel crystal structures were determined during the course of the study. Yellow luminescent complex [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂ was found to be a dimer in the crystal structure. A second crystalline version of this dimer complex, [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂·0.5CH₂Cl₂, was found to be a dichloromethane solvate. However, the luminescence of this solvate was found to be of lower intensity.

[Cu₂(PPh₃)₄(mDCB)₂(BF₄)]ₙ and [Cu₂(PPh₃)₄(pDCB)₂(BF₄)]ₙ·CH₂Cl₂ structures were found to be 1D chain polymers. Lastly, the [Cu₃(PPh₃)₆(mCPy)₃]₃(BF₄)₃ crystal structure showed a trimeric structure, wherein three identical copper(I) center tetrahedron units were linked together.

Film casting of [Cu₂(PPh₃)₄(oDCB)₂](BF₄)₂ from both dichloromethane and chloroform solvent have been studied. Well-cast neon yellow films were exposed to several volatile organic compounds to verify the potential of this brightly luminescent dimer as a chemical sensor. In both cases, exposure to acetone, ethyl sulfide and ether produced no change to the emission of the films. Also, in both cases, exposure to acetonitrile, morpholine and tetrahydrothiophene turned the fluorescence off. However, the rest films exposure to VOCs had the emission
wavelengths in blue-green and yellow-orange ranges.

Further investigations might focus on the crystal structures of metal-organic complexes after exposure to volatile organic solvents. Also, new films needed to be casted with \([\text{Cu}_2(\text{PPh}_3)_4(m\text{DCB})_2(\text{BF}_4)]_n\), \([\text{Cu}_2(\text{PPh}_3)_4(p\text{DCB})_2(\text{BF}_4)]_n\cdot\text{CH}_2\text{Cl}_2\) and \([\text{Cu}_3(\text{PPh}_3)_6(m\text{CPy})_3]_3(\text{BF}_4)_3\) in order to expose them to volatile organic solvent in an effort to find potential chemical sensor materials.
References


9. Fujisawa, Kiyoshi, et al. "M–S vibrational study in three-coordinate thiolato compounds (NEt 4) 2 [M (SC 6 H 4-p-X) 3] and (NEt 4) 2 [M 4 (μ-SC 6 H 4-p-Cl) 6]: M= Cu (I) and Ag (I), X= Cl and Br." *Journal of Inorganic Biochemistry* 82.1 (2000): 229-238.


