Temperature-Compensated Pressure-Sensitive Paint Containing a Bichromophoric Luminophore

Final Report

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The contractor, NanoSonic, Inc., hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. ~~FA9550-C-~~ FA9550-04-C-0100 is complete, accurate, and complies with all requirements of the contract.

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14. ABSTRACT

The effort that has been undertaken during this Phase I STTR program will enable NanoSonic and their academic partner at the University of Dayton to readily move toward commercialization of a sensor paint during Phase II. A bichromophoric compound containing a pressure-sensitive chromophore and a temperature-sensitive chromophore has been synthesized and formulated into a paint. The luminescent intensity response of the temperature sensor was characterized by fluorescence spectroscopy and was found to be linear in the specified temperature range. The luminescence intensity from the pressure sensor emission peak was found to be temperature independent. In addition, communications with Northrop Grumman during Phase I have lead to a partnership for independent testing of the sensor paint in a development wind tunnel.

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1.0 Technical Objective and Rationale

The technical objective of the Air Force STTR Phase I contract FA9550-C-0100 to NanoSonic, Inc. entitled "Temperature Compensated Pressure-Sensitive Paint Containing a Bichromophoric Luminophore" was to develop a temperature and pressure-sensitive paint that can be measured using life-time based methods with pulse illumination to monitor surface response. Illumination of the paint around 460 nm was desired and emission of the two probes at a single wavelength band preferred. The developed paint should have sensitivity in the pressure range from 20-2100 psf and in the temperature range of 5-50 °C. The program ran from 01 September 2004 to 30 May 2005. This is the final report.

The majority of the work conducted on this Phase I STTR program focused on the synthesis of a biluminophore sensor compound. The biluminophore is a complex that contains a temperature sensitive photoluminescent moiety and a pressure sensitive photoluminescent moiety in a single complex. This approach allows for a known amount of both materials to be uniformly dispersed throughout the paint. The temperature sensor used in this study was based on a europium dione. Two different pressure sensors that were investigated during this effort were based on porphyrin and ruthenium-pyridyl sensor compounds. The greatest challenge for this program was to bridge the two different sensors into one compound and to tailor the molecule so that both sensors emit in the same spectral region. A significant advantage of this approach over that of simply blending two separate indicator molecules is the assurance of homogeneous coverage on the test model surface.

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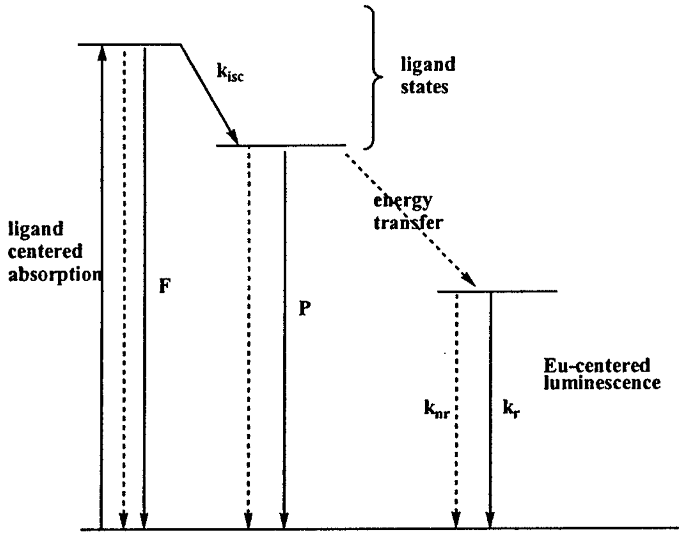


Figure 1-1. Energy level diagram demonstrating the mechanism of photoluminescence for a temperature sensor compound.

Europium based compounds have been widely utilized in temperature sensitive paints.[1-3] The most common is the chelate Europium thenoyltrifluoroacetonate ($Eu(TTA)_3$). When irradiated the TTA dione becomes excited and transfers its energy to the Eu^{3+} ion, Figure 1-1. The observed temperature dependent fluorescence peak at 613 nm is a result of the $^5D_0 \rightarrow {}^7F_1$ transition of the europium ion. The mechanism for temperature dependent fluorescence can be attributed to an increase in non-radiative decay processes through coupling of electronic energy levels to the surroundings through molecular vibrations. Thermal quenching of the excited states is found at both the ligand and at the Eu ion.[4] Furthermore, in Eu chelates containing fluorinated ligands, the onset of increased non-radiative decay occurred at a higher temperature than non-fluorinated substituents yielding temperature sensitivity of fluorescence at and above room temperature. Another study found that the $Eu(TTA)_3$ emission band could be further enhanced when the complex was coordinated to a pyridine based ligand.[5] An example of this type of temperature sensor was found in the literature where $Eu(TTA)_3$ was coordinated to 1,10-phenanthroline. The main fluorescence emission band remained at 613 nm and was shown to have temperature sensitivity from approximately 20 -100 °C.[3]

The mechanism for pressure detection in a pressure sensitive paint relies on the ability of oxygen to quench the triplet-excited state of the photoluminescent sensor which rapidly depletes the excited state population resulting in loss of luminescent intensity and shorter excited state lifetime, Figure 1-2. This measurement technique assumes that the pressure over the binder of the paint is related to the amount of dissolved oxygen in the binder. Therefore, oxygen

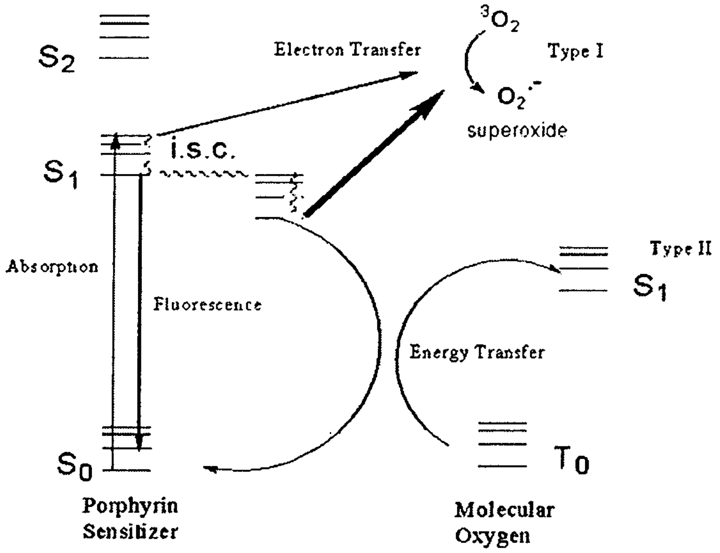


Figure 1-2. Jablonski diagram for the oxygen quenching of the photoexcited state of a pressure sensor compound.

permeability of the binder is essential for sensor response. Porphyrin and ruthenium compounds were investigated as the pressure sensor in the development of a bichromophore compound.

Porphyrins containing platinum metal centers have been used as oxygen sensors and for pressure sensing compounds in paints.[6-9] One of the more common is platinum tetrakis-pentafluorophenyl porphyrin (Pt-TFPP). Pt-TFPP has an absorption peak maximum at 390 nm and displays an emission peak at 650 nm.[8] To assemble a bichromophoric sensor compound, one or more of the pentafluorophenyl groups in the meso position of the porphyrin were substituted with a pyridyl group. This will result in a site for the attachment of the europium temperature sensor. Substitution of porphyrin periphery groups with pyridine or other coordinating groups can be applied to other porphyrins to build a bichromophoric compound. During this program, this approach was applied to two porphyrins, tetrakis-pentafluorophenyl porphyrin and tetraphenyl porphyrin.

Similarly, excited state ruthenium complexes are easily quenched by oxygen and have been studied as pressure sensors.[10-13] In compounds such as ruthenium tris(4,7-diphenyl-1,10-phenanthroline) (Ru-dpp), the phenanthroline group can be substituted with bipyridine or bipyrimidine as a site for temperature sensor attachment in a bichromophoric compound. Ru(dpp) has been reported to have a wavelength of emission at 620 nm when excited at 450 nm.[10] During this Phase I program attempts were made to bridge ruthenium terpyridine or ruthenium bis-bipyridine to Eu(TTA)$_3$ using bipyrimidine. This approach was taken due to the fact that two synthetic pathways could be used to achieve the target compound, either the bridging ligand could be coordinated to the ruthenium terpyridine or ruthenium bis-bipyridine prior to reaction with Eu(TTA)$_3$ or the bridging ligand could be coordinated to the Eu(TTA)$_3$ prior to reaction with the ruthenium complex. All synthetic schemes are discussed in detail in Section 3.0.

2.0 Phase I Technical Tasks

This section will summarize the efforts and results for Technical Tasks undertaken during the Phase I STTR program.

Task 1 Synthesis of a bichromophoric temperature and pressure sensor compound.

The syntheses of all complexes were conducted at the University of Dayton Department of Chemistry under the direction of Dr. Shawn Swavey. Considerable effort was spent during this program on the synthesis of the bichromophoric luminophore. The synthesis of a pyridyl substituted pentafluorophenyl porphyrin pressure sensor was successful but the anticipated attachment of europium thenoyltrifluoroacetonate (Eu(TTA)$_3$)temperature sensor did not occur due to solubility issues between the two components. A second pyridyl substituted porphyrin was synthesized containing phenyl substituents. This compound was successfully reacted with Eu(TTA)$_3$ and the resulting complex was characterized and tested for temperature sensitive luminescence.

A separate synthetic effort focused on bridging ruthenium-based pressure sensors to the europium TTA temperature sensor. In these experiments, attempts were made to bridge ruthenium terpyridine or ruthenium bisbipyridyl with Eu(TTA)$_3$ using bipyrimidine. The ruthenium chelate was successfully reacted with the bipyrimidine, but the resulting complex was unreactive towards Eu(TTA)$_3$. Attempts to attach the bridging ligand to the Eu(TTA)$_3$ portion of the target bichromophoric compound resulted in the bimetallic (TTA)$_3$Eu-bpm-Eu(TTA)$_3$ complex. This compound was purified, characterized, and tested for temperature sensitive photoluminescence. Results of the di-europium compound were compared to a (TTA)$_3$Eu-bipyridine complex synthesized in-house.

Task 2 Formulation and spray application of sensor paint.

Formulation and application of the sensor paint developed for analysis of the luminescence temperature response of compounds synthesized in Task 1 was successfully accomplished with assistance from the University of Dayton Research Institute. A nitrocellulose binder was chosen for the binder to ensure solubility of the sensor compounds in the binder. Three formulations containing (TTA)$_3$Eu-bipyridine, (TTA)$_3$Eu-bpm-Eu(TTA)$_3$, or triphenylporphyrin-pyridine-

Eu(TTA)3 were successfully spray coated onto epoxy-primed aluminum substrates to enable subsequent experimental evaluation.

Task 3 Measurement of luminescent pressure response of coated sensor paint. During this Phase I effort, paints were not evaluated for the sensitivity of luminescence toward pressure. However, solution fluorescence of the triphenylporphyrin-pyr- Eu(TTA)3 complex indicated that two separate emission peaks were present when the compound was excited at 420 nm. Further development is suggested as part of Phase II materials optimization to verify sensitivity of the emission peaks toward oxygen quenching. In order to evaluate this response in the sensor paint, an alternate binder having higher oxygen permeability will need to be identified.

Task 4 Temperature-dependent studies of the bichromophore luminescence. The monometallic and bimetallic europium compounds synthesized in Task 1 were successfully evaluated for temperature-sensitive luminescence in solid form. Solid samples were achieved by evaporating a solution of the compound onto an epoxy-primed substrate. In addition, the bichromophoric triphenyl pyridylporphyrin-Eu(TTA)3 complex, mono-metallic and bi-metallic europium (TTA)3 sensor compounds immobilized in a nitrocellulose binder prepared in Task 2 were evaluated in the same manner.

Dr. Karen Brewer of the Department of Chemistry at Virginia Tech (VT) graciously assisted in the experimental evaluation of the paint formulations. Samples were evaluated for photoluminescence emission by the use of PTI Alphascan fluorometer. A heat block designed for a separate temperature-sensitive paint development program built by the machine shop at VT to fit within the optics of the fluorometer was used to conduct temperature response studies. The heater utilized a temperature controller, heater, and temperature probe from Omega Instruments and can withstand temperatures up to 100 °C.

Evaluation of the fluorescence intensity of the bichromophoric luminophore synthesized for this program containing a triphenyl porphyrin coordinated to Eu(TTA)3 through a pyridyl group indicated that the porphyrin displayed two emission bands. The peak centered at 615 nm is associated with emission from the europium temperature sensor and the peak centered at 650 nm is associated with the porphyrin pressure sensor. Both peaks could be excited at 340 nm or 420 nm. The emission band at 615 nm was more sensitive to temperature effects when the film was excited at 340 nm as compared to excitation at 420 nm. In addition, the peak at 650 nm was more stable to temperature effects when irradiated at 340 nm as compared to 420 nm. This indicates that in this compound, temperature dependence of the pressure-sensitive component can be minimized by choosing a higher energy excitation source. This is significant because no correction for temperature effects on intensity will be needed for the evaluation of fluorescence intensity response to pressure.

In addition to the evaluation of the porphyrin-europium bichromophore, the effect of changing temperature on fluorescence intensity was evaluated for a bi-metallic europium $(TTA)_3$ compound that was synthesized for this program. Fluorescence response was also evaluated for a mono-metallic europium analog for comparison. The fluorescence data indicates that there was increased sensitivity to change in temperature in the range of 23-100 °C for the bimetallic compound. This is important to extend the testing range of the temperature sensor.

Task 5 Develop commercial partnerships for Phase II process scale-up, application and testing.

During the Phase I program period, NanoSonic discussed the technical results and Phase II development plan with several major defense contractors, including Lockheed Martin Skunk Works in both Palmdale, CA, and Marietta, GA, Boeing Phantom Works in St. Louis, MO, and Mesa, AZ, and Northrop Grumman Aircraft Systems Division in El Segundo, CA. The materials and instrumentation group at Northrop Grumman is highly interested in our demonstrated results, in part because this effort relates in part to other cooperative materials work we have underway. We anticipate that for a possible Phase II STTR program, Northrop Grumman would work with us on a small subcontract basis to perform experimental materials evaluation in their El Segundo facility.

3.0 Experimental

This section will detail experimental procedures and spectroscopic set up used during the Phase I efforts for this program. For analysis of the synthesized sensor compounds the following instruments were utilized: UV-vis spectra were taken using a Schimadzu 1501 photodiode array spectrophotometer, solution fluorescence measurements were taken using Cary Eclipse Fluorescence Spectrophotometer, proton NMR was conducted using Bruker 300 MHz spectrophotometer and cyclic voltammetry was conducted using a CH Instruments 630A electrochemical analyzer.

3.1 Synthesis and analysis of porphyrin-based sensor compounds

Synthesis of pyridyl-substituted porphyrins

For this program, two target porphyrins having pyridyl groups in the meso position were synthesized, one containing pentafluorophenyl groups and the

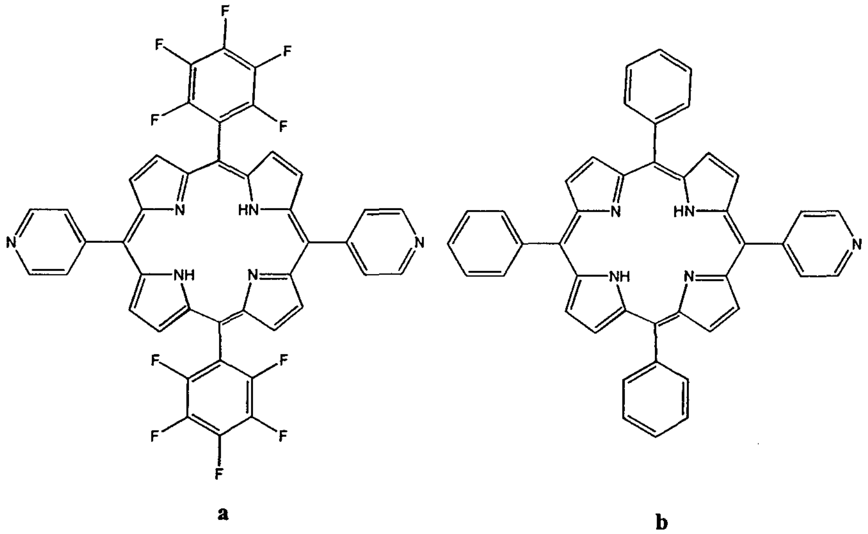
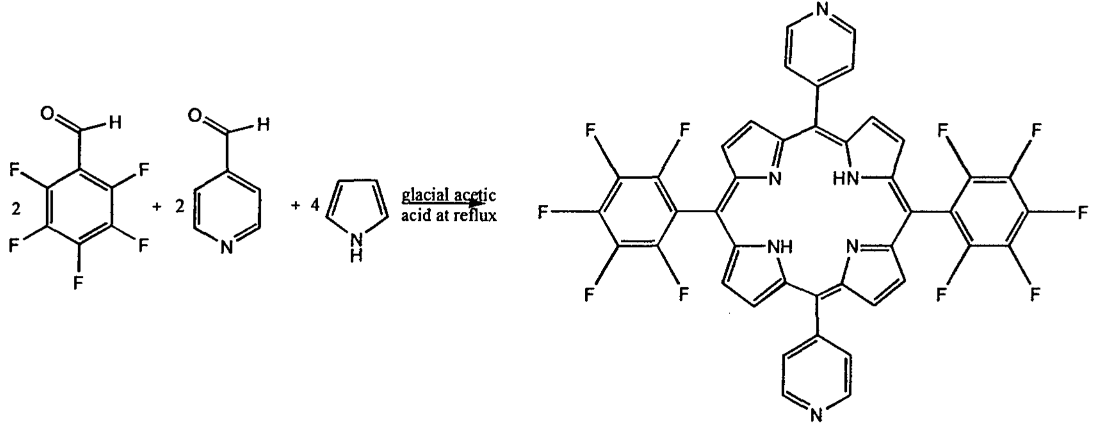


Figure 3-1. Target porphyrin compounds containing pyridine bridging ligand. (a) trans bipyridyl bipentafluorophenyl porphyrin, (b) triphenyl monopyridyl porphyrin.

second containing phenyl groups, Figure 3-1. The general reaction for both porphyrins can be found in Scheme 3-1. During the reaction, the stoichiometry of the reactants is chosen in order to favor a mono-, bi-, or tri-pyridyl substituted porphyrin ring. The reaction that favors a trans-bi-pyridyl-bi-pentafluorophenyl porphyrin is illustrated. This compound has two sites for attachment of a temperature sensor. The synthetic scheme was derived from literature reported preparation similar porphyrins.[14]



Scheme 3-1. Synthetic approach to the trans-pyridyl porphyrin.

The synthesis of porphyrins results in numerous byproducts, such as polymeric side products as well as a number of porphyrins. Exhaustive purification is needed to ensure isolation of the desired products. The polymeric by-products are removed through neutralization and hot water washings and the crude porphyrins separated by column chromatography. It is essential and somewhat

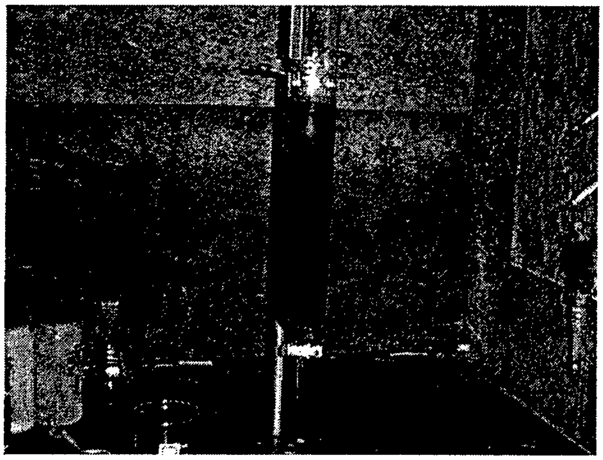


Figure 3-2. Chromatographic separation of porphyrins.

time consuming to choose the correct solvent combination for maximum separation. Once a solvent system is identified the porphyrins are separated on a silica column as shown in Figure 3-2. The different red bands represent different porphyrins. Once isolated the porphyrins are characterized by ^{1}H NMR and UV/visible spectroscopy.

The reaction shown in Scheme 3-1 yielded small quantities of the trans-bi-pyridyl-bi-pentafluorophenyl porphyrin. The tri-pyridyl-mono-pentafluorophenyl porphyrin was isolated in much larger quantities and was used to react with europium to produce a bimetallic sensor compound. The latter compound and its UV-visible spectrum can be found in Figure 3-3 having a strong absorption band centered at 450 nm.

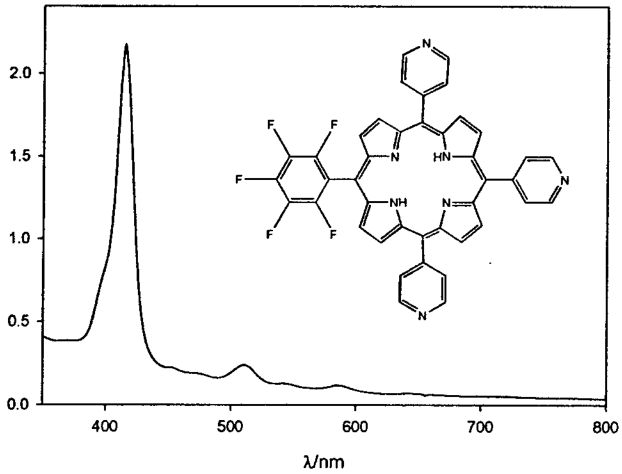
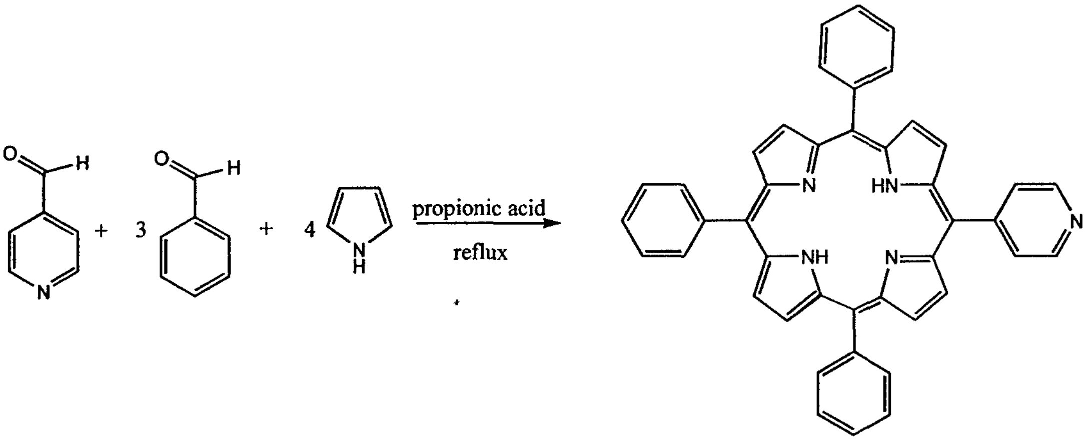


Figure 3-3: UV-visible spectrum of tri-pyridyl-mono-pentafluorophenyl porphyrin.

A similar procedure was used to produce a pyridyl substituted phenyl porphyrin. For this reaction the stoichiometry of the reactants was chosen to favor a mono-pyridyl-tri-phenyl porphyrin, Scheme 3-2. The reaction produced six porphyrins and the mono-pyridyl substituted porphyrin was isolated in good yields from column chromatography. UV-visible spectroscopy of the resulting porphyrin showed a strong absorption band at 420 nm. This porphyrin was also reacted with europium to attempt to synthesize a bichromophoric complex.

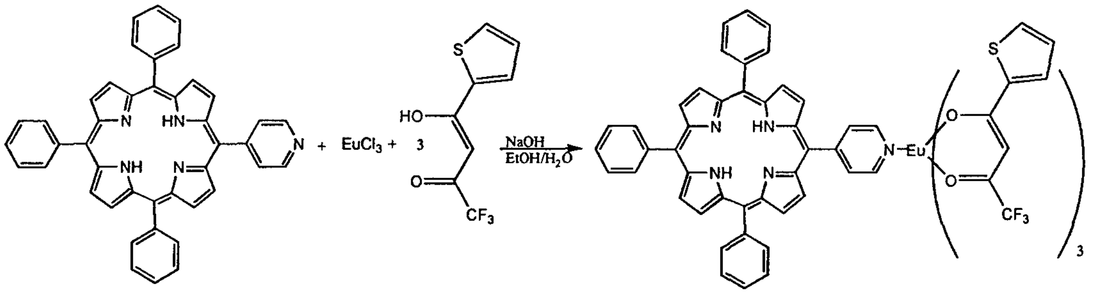


Scheme 3-2. Synthetic approach to monopyridyl triphenyl porphyrin.

Synthesis of bichromophoric Porphyrin/Europium complex

Attempts were made to form a bichromophoric porphyrin/europium complex using the tri-pyridyl-mono-pentafluorophenyl porphyrin described above. The tri-pyridyl-mono-pentafluorophenyl porphyrin was reacted with europium trichloride and 4,4,4-trifluoro(1-(2-thenly)-1,3-butadione in procedure adapted from literature. [3] Harsh reaction conditions and poor solubility of the porphyrin yield no attachment of the europium to the porphyrin pyridyl groups.

A second attempt was made for the formation of a bichromophoric complex using the mono-pyridyl-tri-phenyl porphyrin. For this attempt, the purified porphyrin was reacted at room temperature in a 1:1 ratio with commercially available Eu(TTA)$_3$ dissolved in chloroform, Scheme 3-3. The product was precipitated from the reaction mixture by addition of hexanes, and was filtered and dried. In order to verify the reaction occurred, UV-visible spectra were taken of the starting reagents and the product. The spectra can be found in Figure 3-4. The product porphyrin-Eu(TTA)$_3$ complex showed two strong absorbance peaks, a broad band centered at 340 nm associated with the europium group and a sharp peak centered at 420 nm associated with the porphyrin ring. The UV-visible spectrum of the product does not show any shift of the starting reagent's bands indicating that there is very little electronic interaction when the europium is coordinated to the porphyrin.



Scheme 3-3. Synthetic scheme for the formation of a porphyrin-europium bridged bichromophoric complex.

Fluorescence spectroscopy was also used to analyze the complex in solution. When excited at 340 nm, two emission bands were found, one centered at 615 nm associated with the Eu(TTA)3 portion of the compound and the second centered at 650 nm resulting from the excitation of the porphyrin. The spectrum is shown in Figure 3-5 (a). In addition, when the complex is excited at 420 nm, only the emission peak at 650 nm is found, Figure 3-5 (b). This indicates that excitation of the mono-pyridyl-tri-phenyl porphyrin-Eu(TTA)3 complex at 340 nm will allow for luminescence of both chromophores. In the scope of this program, it is desired to utilize one excitation source as well as design a compound that emits in the same spectral region. Future work will focus on shifting the peak maximum of the temperature sensor to lower energy and/or shifting the peak maximum of the porphyrin pressure sensor to higher energy for better spectral overlap.

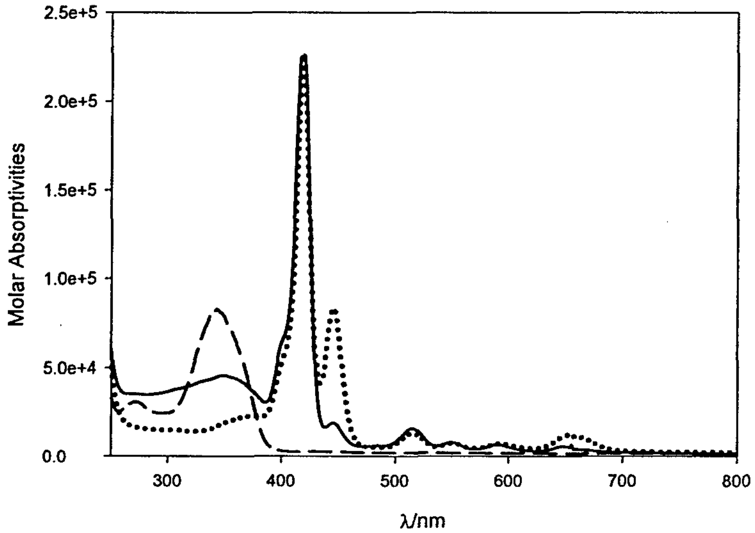


Figure 3-4. UV-visible spectra of mono-pyridyl-tri-phenyl porphyrin (dotted line), Eu(TTA)3 (dashed line), and porphyrin-pyr-Eu(TTA)3 (solid line).

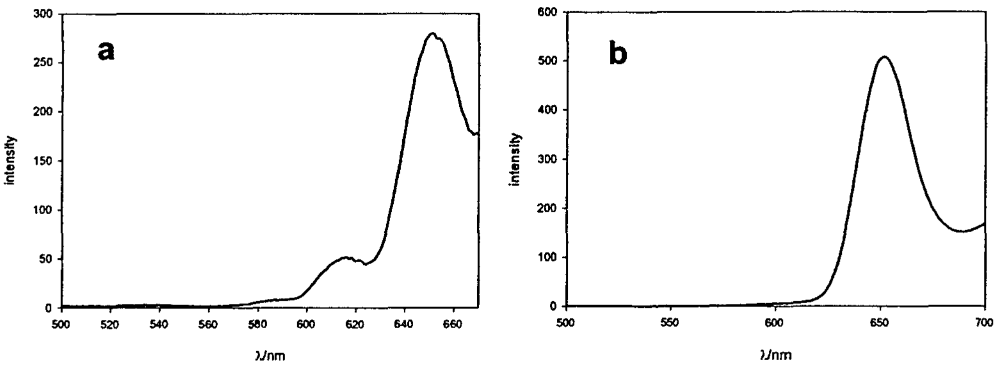
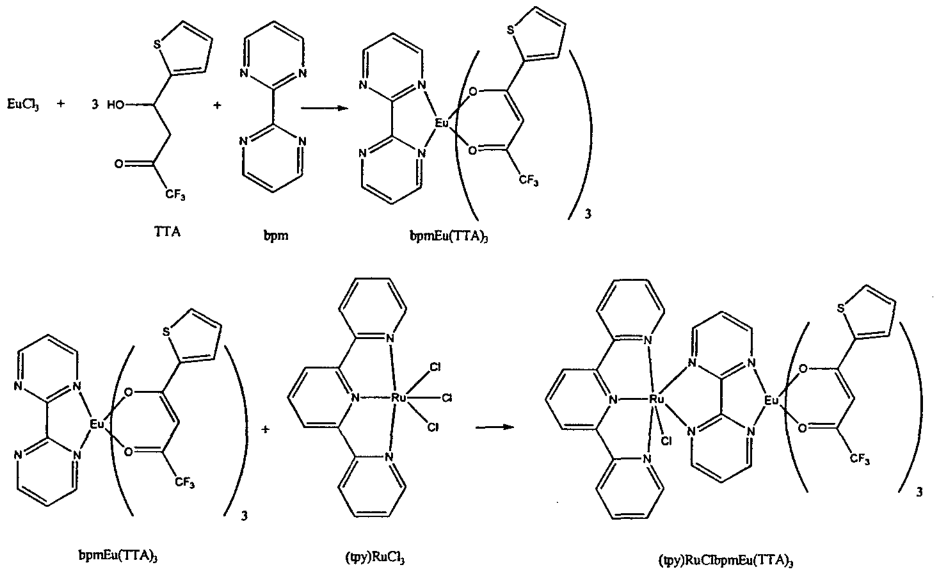


Figure 3-5. Fluorescence spectra of porphyrin-Eu(TTA)$_3$ excited at (a) 340 nm and (b) 420 nm.

3.2 Synthesis of ruthenium-based sensor compounds

Pressure-sensitive paints based on ruthenium (II) polypyridyl pressure sensors have been investigated for many years. [10-13] For this application, a novel complex containing ruthenium (II) 2,6:2′,2″-terpyridine and europium (III) 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadione (TTA) bridged by a bipyrimidine ligand was proposed, Scheme 3-4.



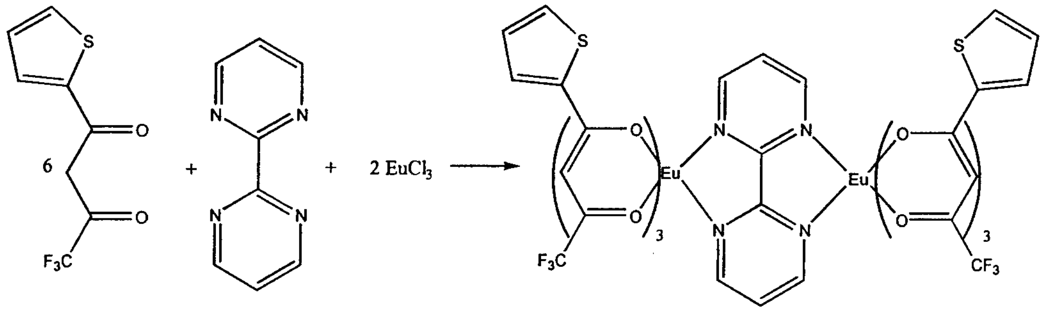
Scheme 3-4: Synthesis of bpmEu(TTA)$_3$ and (tpy)RuClbpmEu(TTA)$_3$ sensor complexes.

The synthetic procedure for the europium-TTA complex containing the bridging bipyrimidine ligand was adapted from a literature procedure.[3] The reaction yielded a white powder that was recrystallized from ethyl acetate and hexane, line 1 of Scheme 3-2. This compound was reacted in acetonitrile with ruthenium

(II) 2,6:2′,2″-terpyridine trichloride in the presence of base under reflux for 6 hours.[15] The product was isolated as an orange powder.

After further purification, the target complex was analyzed by elemental analysis of C, H, N, S, and F. The results indicated that the Ru-Eu bridged complex was not achieved, but instead formation of a bimetallic europium complex, $(TTA)_3EubpmEu(TTA)_3$ resulted from the reaction in the first step of Scheme 3-4. Attempts were made to synthesize the mono-Eu complex $bpmEu(TTA)_3$ by adjusting reaction conditions and reactant stoichiometry but all attempts yielded the bimetallic europium complex.

The di-europium$(TTA)_3$ bridged compound was also directly synthesized as illustrated in Scheme 3-5. Solution UV-visible spectrum of the di-europium bridged complex in chloroform indicated a strong a absorption at 350 nm, Figure 3-6a. The fluorescence spectrum measured for this solution can be found in Figure 3-6b. The solution was excited at 350 nm and the spectrum collected from 500-640 nm. A strong, sharp emission band was found at 615 nm.



Scheme 3-5. Synthetic scheme for the formation of $(TTA)_3$Eu-bpm-Eu$(TTA)_3$.

A second attempt was made to isolate a mono-europium/bridging ligand compound by substituting dipyridyl-pyrazine (dpp) for bipyrimidine as the bridging ligand. This bridging ligand was chosen due to the fact that dpp contains low-lying π* orbitals resulting in a greater pathway for radiative decay in the Eu-complex. Various reaction conditions were attempted but no reaction between europium trichloride and the dipyridyl-pyrazine was found. It was speculated that the basicity of the pyrizine nitrogens prevented the reaction from occurring.

Due to the fact that the mono-europium-bridging ligand complex could not be isolated, an alternate route to the formation of a bimetallic ruthenium-europium $(TTA)_3$ complex was taken. In this reaction pathway, the bridging ligand, bipyrimidine (bpm), was first coordinated to the Ru metal prior to reaction with

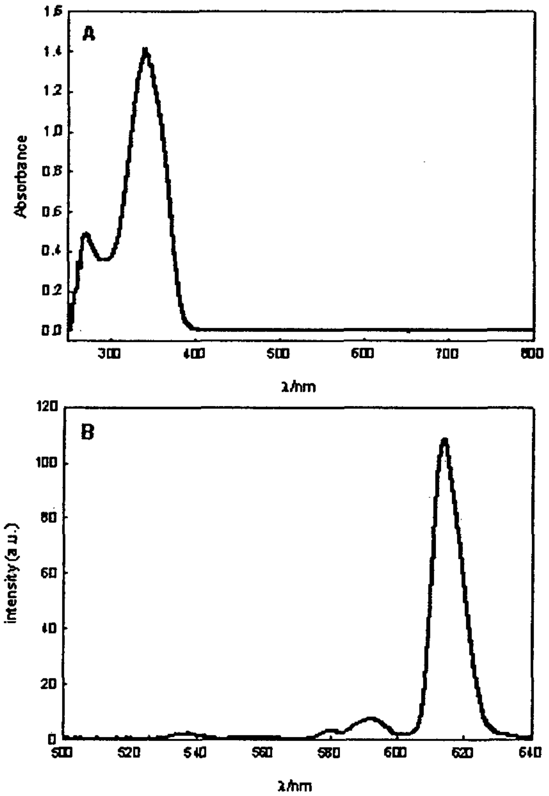
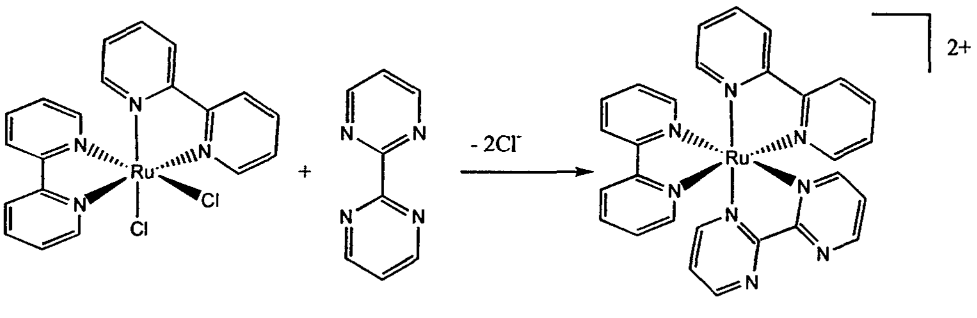


Figure 3-6. UV-visible spectrum (a) and fluorescence emission spectrum (b) of a solution of $(TTA)_3$Eu-bpm-Eu$(TTA)_3$ in chloroform.

europium, Scheme 3-6. An alternate ligand was chosen for the ruthenium center in order to change the geometry around the metal, two bipyridine (bpy) ligands were coordinated to the Ru instead of terpyridine. The procedure for the formation of $(bpy)_2$Rubpm was adapted from literature, and the product was successfully precipitated as the PF_6 or chloride salt. [16] In addition, (terpyridine)Rubpm was synthesized in a similar fashion.



Scheme 3-6. Synthesis of $(bpy)_2$Rubpm.

Table 3-1: Outline of bi-metallic Ru-Eu reactions investigated.

#	Ru reactant	Ru salt	Eu reactant	Solvent
1	$(bpy)_2$Rubpm	PF_6	$Eu(TTA)_3$	EtOH
2	$(bpy)_2$Rubpm	PF_6	$Eu(TTA)_3$	CH_2Cl_2
3	(tpy)Rubpm	PF_6	$Eu(TTA)_3$	CH_2Cl_2
4	$(bpy)_2$Rubpm	2 Cl	$EuCl_3$ + 3TTA	EtOH

Table 3-1 outlines various reactions of ruthenium-bpm complex with europium. All reactions failed to result in the bimetallic Ru-Eu bichromophore. In some reactions, the ruthenium compound containing the bridging ligand was reacted with commercially available europium thenoyltrifluoroacetonate, and in other reactions with europium trichloride and thenoyltrifluoroacetonate. Various solvents were also chosen in attempt to overcome solubility issue between reactants. A literature search revealed a paper that successfully reacted a rhenium diimine with lanthanides using dichloromethane as the reaction solvent and precipitation the product using hexanes. [17] Two reactions were attempted adopting this reaction procedure but both failed due to limited solubility of the ruthenium reactant in methylene chloride. The reactions were attempted once again using acetonitrile as a co-solvent, but the reaction did not proceed.

3.3 Paint formulation and spray application

Paint formulations were blended and applied under the supervision of Bill Culhane at University of Dayton Research Institute. Coated samples were prepared by applying a binder containing the photoluminescent compound to primed aluminum panels. 2024 T-3 bare aluminum panels were originally pretreated with Alodine 1200S, a chromate conversion coating used to reduce corrosion. The pretreated panels were primed with approximately 1.4 mil dry of a white, two-part epoxy conforming to Mil-P-53022B.

A number of binder formulae were investigated to fully dissolve the photoluminescent sensor compounds, and a nitrocellulose polymer plasticized with dibutyl phthalate and dissolved in butyl acetate, ethyl acetate and isopropyl alcohol was found to be compatible. The coating formula, commercially available under the trade name "In a Hurry Dry Topcoat", is readily miscible in ethyl acetate and methylene chloride, the solvents used to dissolve the temperature sensor compounds.

Table 3-2 outlines the components of three paint formulations coated during this Phase I effort. To prepare the paint, 10.0 grams of binder formula (2.0 grams dry) were weighed into a beaker for each sample. A solution containing 10 milligrams of the sensor compounds was added to the beaker with stirring.

Finally the sample was diluted to approximately 25 milliliters with additional methylene chloride. The coating formulation containing mono-europium(TTA)$_3$ compound became homogeneous almost immediately. It was stirred for approximately 5 minutes and then spray coated. Formulations containing di-europium(TTA)$_3$ and the triphenylpyridyl porphyrin-Eu(TTA)$_3$ sensors initially separated into two phases, but became homogeneous after 30 minutes of stirring.

Paint sample were spray coated onto primed aluminum panels using a Central Pneumatic Touch-up spray gun. 25 PSI of air pressure was used and the fluid flow and nozzle were adjusted to give the best fan pattern. The number of passes varied with the coating formulation. Coated substrates were air dried under ambient conditions.

Table 3-2. Temperature-sensitive paint formulations.

Formulation Components	Mono-europium Complex	Bi-europium Complex	Porphyrin-$Eu(TTA)_3$
Nitrocellulose polymer	2.0 grams	2.0 grams	2.0 grams
Sensor Compound	10 milligrams	10 milligrams	10 milligrams
Methylene chloride	14 grams	13 grams	15 grams
Ethyl acetate	4 to 5 grams	4 to 5 grams	3-4 grams
Butyl acetate	4 to 6 grams	4 to 6 grams	4 to 6 grams
Dibutyl phthalate	1 to 2 grams	1 to 2 grams	1 to 2 grams
Camphor	0.5 to 1 gram	0.5 to 1 gram	0.5 to 1 gram

3.4 Spectroscopic Analysis

Dr. Karen Brewer and her group at Virginia Polytechnic Institute and State University Department of Chemistry conducted spectroscopic analysis of paint components and formulations. The emission system utilized for the detection of photoluminescence emission and response to variable temperature was a PTI Alphascan fluorometer. The Alphascan was equipped with single photon counting, modified to detect red shifted and low intensity emissions, and is capable of right angle and front face emission measurements. The optical layout is shown below, Figure 3-7. The design of the variable temperature cell holder accommodates the coated Al samples and allows for front face emission measurements at variable temperature, Figure 3-8. The sample for analysis was placed in the variable temperature cell holder mounted a conducting block in contact with heating pad controlled by an Omega temperature controller. Read out of the temperature was accomplished through a thermocouple in contact with the conducting block adjacent to the sample. Accuracy of the measured temperature at the sample surface was within 2 degrees Fahrenheit of that measured within the conducting block.

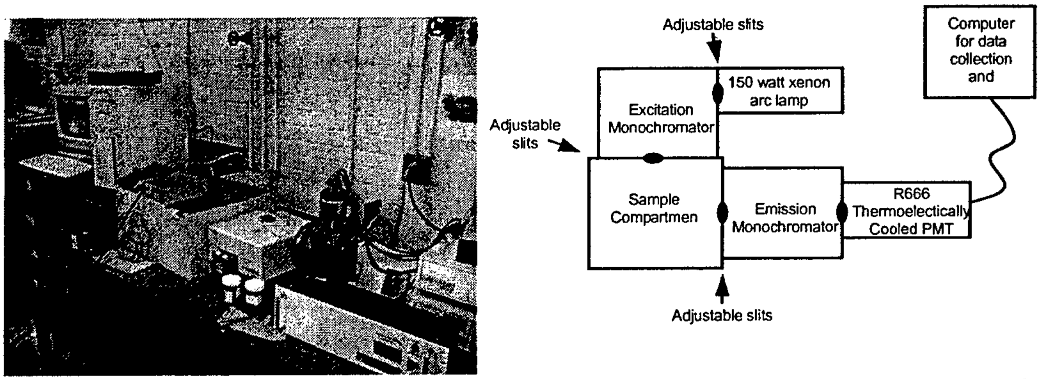


Figure 3-7. Experimental set up of the PTI Alphascan fluorescence spectrometer used to evaluate photoluminescence emission.

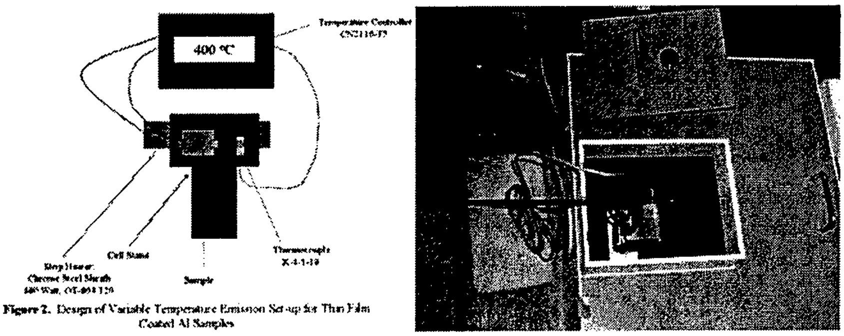


Figure 3-8. Diagram of the variable temperature cell mounted in the PTI Alphascan fluorometer.

4.0 Results and Discussion

The experimental synthetic lab work for this Phase I STTR program demonstrated the ability to synthesize unique luminescent sensor compounds and formulate them into a binder to produce a paint that can be applied by spray coating. The sensitivity of the luminescent emission towards changes in pressure and temperature needs to be examined. After the sensor paint has been established, lifetimes of the excited states needs to be measured for each component and the paint needs to be calibrated. During this Phase I effort, fluorescence spectroscopy was used to measure the emission spectrum of the temperature- and pressure-sensitive chromophores described in Section 3.1 and 3.2 with changing temperature. Further work is still needed to characterize the emission spectrum with changing pressure and to calibrate the paint. This section below details the results of the variable temperature fluorescence emission experiments.

4.1 Temperature-dependent luminescence of bichromophoric porphyrin-Eu(TTA)$_3$ complex

A bi-chromophoric sensor compound containing a triphenyl monopyridyl porphyrin, H_2MPyTPP, pressure sensor and a europium tris-(trifluorothienoyl acetonate), Eu(TTA)$_3$, temperature sensor was developed during this Phase I program, Figure 4.1. The fluorescence emission spectrum for this compound when excited at 340 nm reveals two emission bands, one centered at 615 nm associated with the europium temperature sensor and a second centered at 650 nm associated with the porphyrin pressure sensor. The effect of surface temperature on the intensity of the emission peaks was studied using fluorescence spectroscopy.

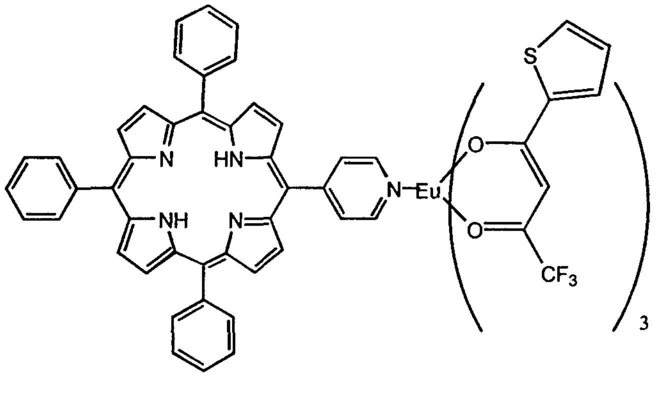


Figure 4-1. Structure of H_2MPyTPP-Eu(TTA)$_3$

For the temperature dependent fluorescence emission study the porphyrin-europium complex was suspended in a nitrocellulose binder and spray coated onto epoxy-primed aluminum panels. The panels were placed onto a sample holder affixed to a copper heating block mounted in the fluorescence spectrometer. The temperature was ramped from 17 to 50 °C and the emission spectrum scanned from 590 nm to 650 nm at 2-4 °C intervals. The rate of heating was chosen such that the surface temperature did not change by more than 1 °C during the scan of the spectral region. A higher temperature could not be achieved due to thermal instability of the nitrocellulose binder.

An overly of the emission spectra is shown in Figure 4-2a. The area under the peak centered at 615 nm was calculated and a temperature profile was generated, Figure 4-2b. In this temperature range the sample showed near linear decrease in intensity of the Eu(TTA)$_3$ peak with increasing temperature. At 50 °C the peak intensity had not dropped to zero. With a more thermally stable binder the temperature profile could be expanded up to 100 °C.

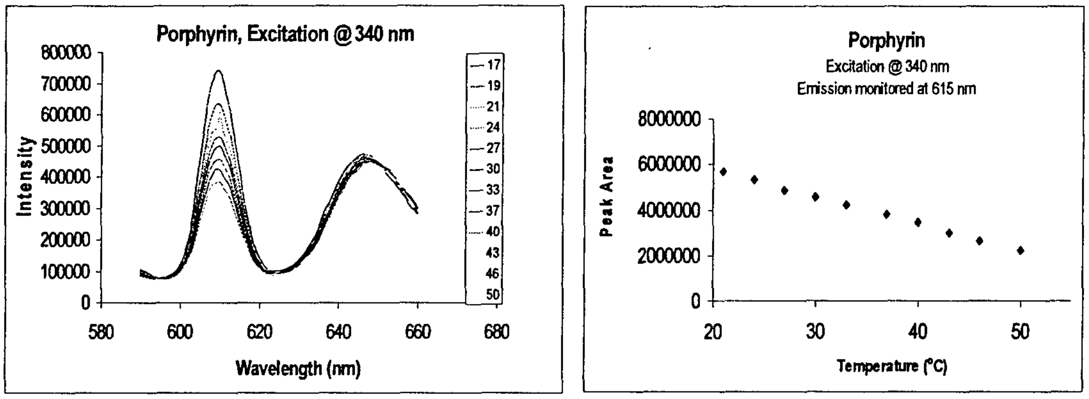
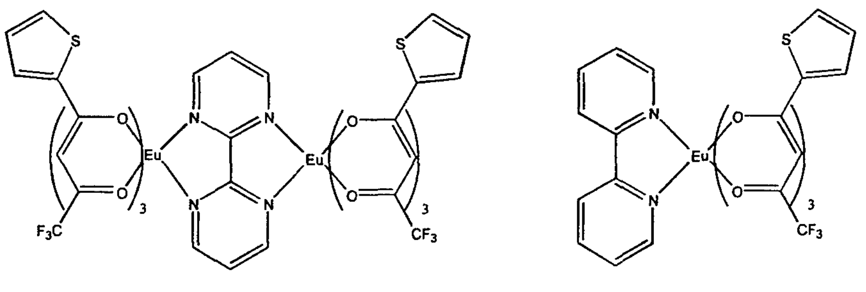


Figure 4-2. Temperature sensitive emission for porphyrin-europium sensor complex, (a) overlay of emission spectra as a function of T, (b) temperature profile of data in (a).

The emission peak for the porphyrin pressure sensor component was also monitored for temperature sensitivity. The peak centered at 650 nm in Figure 4-2a shows no change in intensity in the temperature range examined. This behavior is important so that no correction in emission intensity is needed due to temperature dependence when calibrating the pressure sensor.

4.2 Temperature-dependent luminescence of Eu(TTA)3 complexes

An alternate synthetic route to the formation of a bichromophoric sensor compound yielded a di-europium temperature sensor. The complex is composed of two Eu(TTA)3 temperature sensors bridged by a bipyrimidine ligand, Figure 4.3a. To determine the significance of the two Eu units to the measurement of surface temperature an analogous mono-europium compound was synthesized, bipyridine-Eu-(TTA)3 Figure 4.3b.



(a) (b)

Figure 4-3. Structure of europium based temperature sensors (a) bi-europium (TTA)3EubpmEu(TTA)3 and (b) mono-europium bpyEu(TTA)3.

Initial temperature-dependence of the fluorescence emission peak was evaluated on solid films of the bi- and mono-europium compounds. This was accomplished by evaporating ethyl acetate solutions of the respective europium complexes onto epoxy primed aluminum panels. The panels were mounted onto a copper heating block and placed in the fluorescence spectrometer. The temperature was slowly ramped from room temperature to 110 °C. The samples were photoexcited at 340 nm and the emission spectra scanned from 560 nm - 640 nm every 3-5 °C. This rate of heating was chosen so that the temperature of the sample did not change more than 1 °C during the spectral scan.

An overlay of the spectral scans at various temperatures can be found in Figure 4.4. Both compounds had a sharp emission peak centered at 615 nm that decreased in intensity with increasing temperature. The area under the peaks were calculated and plotted versus temperature. Figure 4.5a shows the temperature profile of the mono-europium, bpy-Eu(TTA)$_3$, and Figure 4.5b shows the temperature profile for the di-europium complex, (TTA)$_3$EubpmEu(TTA)$_3$. Comparison of the two profiles reveals that there is an increase in sensitivity of the di-europium compound. The emission intensity of the mono-europium compound drops to zero at 50 °C, while the di-europium sample does not lose emission intensity until 90 °C.

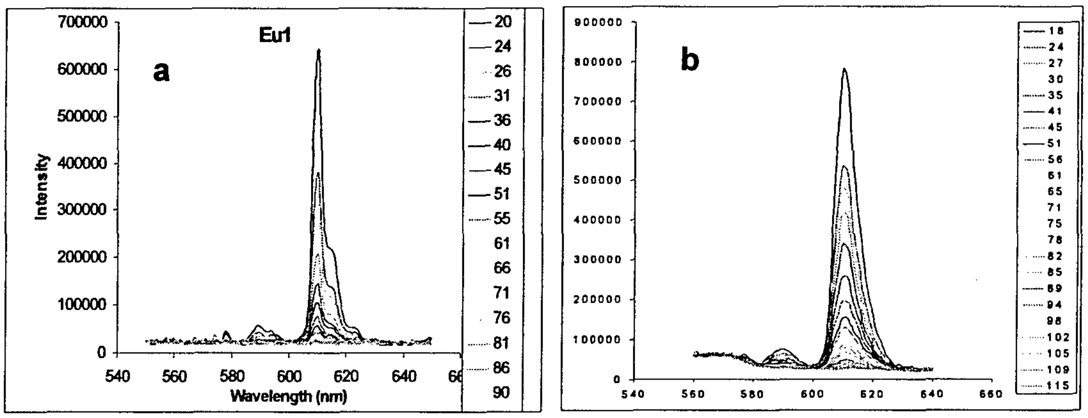


Figure 4-4. Temperature dependent fluorescence emission spectra for (a) bpy-Eu(TTA)$_3$ and (b) (TTA)$_3$EubpmEu(TTA)$_3$. Excitation energy 340 nm.

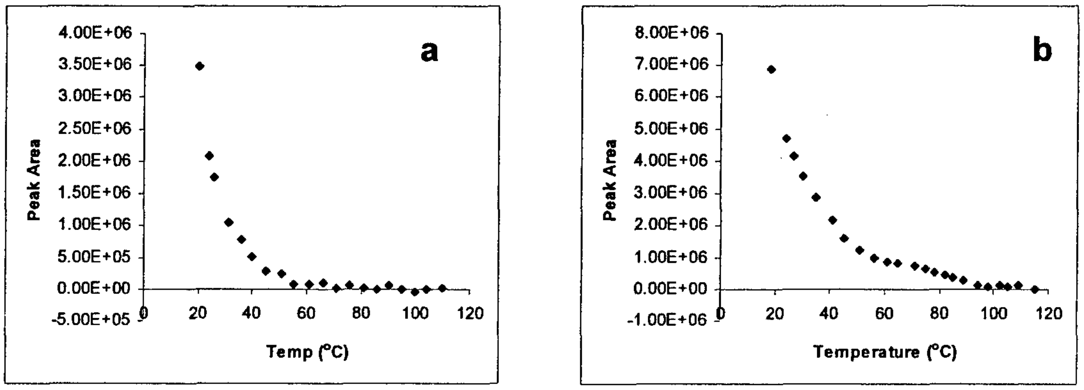
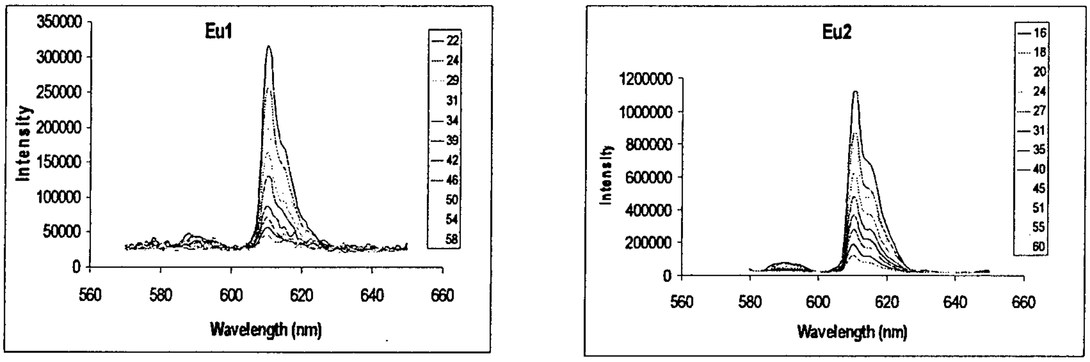


Figure 4-5. Temperature profiles of (a) bpy-Eu(TTA)$_3$ and (b) (TTA)$_3$EubpmEu(TTA)$_3$ showing increased emission sensitivity in the temperature range 50-90 °C.

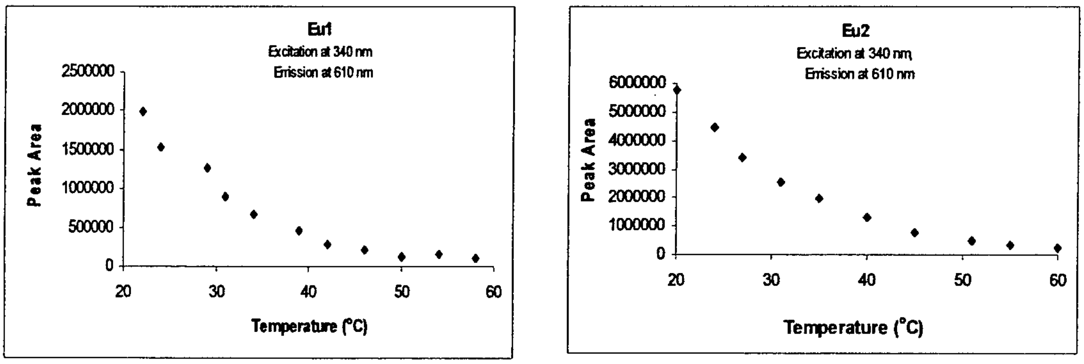
To further analyze the compounds, they were formulated into a nitrocellulose binder. The paint was applied to an epoxy-primed aluminum panel and air dried. The panels were mounted onto a heating stage in the fluorimeter and photoemission was monitored in the spectral region of 570 nm to 650 nm. The variable temperature scans can be found in Figure 4.6 for both compounds. The peak shape at 615 nm had changed once the luminescent compounds were dissolved in the nitrocellulose binder. Integration of the peak area to generate temperature profiles reveals that the added temperature sensitivity of the di-europium complex has been diminished in the paint formulation, Figure 4.7. This is most likely due to break down of the polymer binder which begins to occur at 40 °C. A more robust binder is needed to further evaluate these temperature sensors.



a

b

Figure 4-6. Overlay of fluorescence emission at various temperatures (a) bpy-Eu(TTA)$_3$ and (b) (TTA)$_3$EubpmEu(TTA)$_3$.



a

b

Figure 4-7. Temperature profile for the data in Figure 4.6 (a) bpy-Eu(TTA)$_3$ and (b) (TTA)$_3$EubpmEu(TTA)$_3$.

5.0 Phase II Development and Transition to Commercialization

The Phase I STTR program demonstrated a viable chemical synthesis pathway for the development of temperature- and pressure-sensitive paints. Such paints have a number of potential commercial applications, including use during the development and testing of next generation aircraft.

5.1 Phase II Development Program Rationale

During the Phase I program, NanoSonic has talked with several major U.S. defense and aerospace companies about our sensing paint research. These discussions have occurred as part of other discussions of cooperative materials and systems-level development programs we have underway with Northrop Grumman, Lockheed Martin and Boeing. The materials and instrumentation group we are working with at Northrop Grumman Aircraft Systems Division in El Segundo has expressed significant interest in these materials, in part because of other work we are performing for the Air Force that directly involves their platform applications. During a possible Phase II program, NanoSonic would thus plan to work with our university research partner - the Department of Chemistry at the University of Dayton – to develop, up-scale and characterize in the laboratory a set of sensitive paint prototype materials. These materials would be evaluated in airframe development laboratories at Northrop Grumman through a small subcontract. Eric Barnes' materials group at Northrop Grumman would coordinate this subcontract effort; NanoSonic anticipates that a letter of support for the Phase II effort would come from Eric.

The larger purpose of the subcontract would be to increase the technology readiness level (TRL) of the sensitive paints to the level of having been evaluated under actual systems level laboratory conditions by a prime contractor. This in part would also help justify the transition to commercial production and use of such materials by Northrop Grumman, other aerospace companies, and a broader range of commercial customers.

5.2 Sensitive Paint Commercial Development, Production and Sales

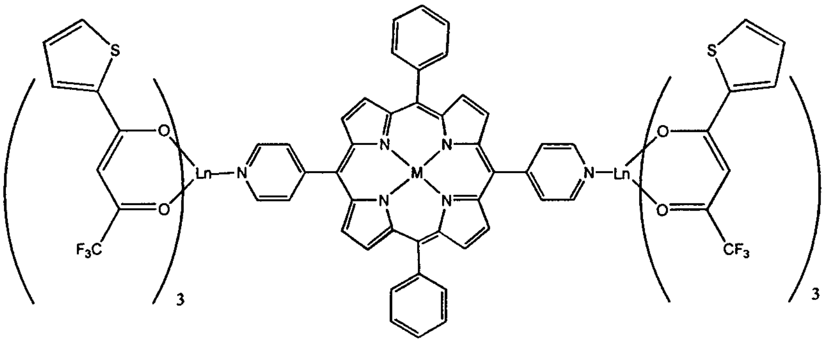
Temperature- and pressure-sensitive paints and coatings have direct applications as a means of instrumentation during the development of aircraft platforms. They also have similar applications for the research and development of propulsion systems, power-generating systems, land vehicles and high performance ships and recreational boats.

NanoSonic has successfully developed other specialized coatings and free-standing nanocluster/polymer materials, including Metal Rubber™, a highly elastic (modulus from less than 1 to greater than 500 MPa) and highly conductive (electrical conductivities as high as 10^{-5} Ωcm) material. Metal Rubber™ has multiple defense system applications; NanoSonic developed out of Air Force and other SBIR research efforts, and currently sells material and works with several major defense primes on its applications to specific platforms.

6.0 Conclusions and Future Work

The effort that has been undertaken during this Phase I STTR program will enable NanoSonic and their academic partner at the University of Dayton to readily move toward commercialization of a sensor paint during Phase II. A bichromophoric compound containing a pressure-sensitive chromophore and a temperature-sensitive chromophore has been synthesized and formulated into a paint. The luminescent intensity response of the temperature sensor was characterized by fluorescence spectroscopy and was found to be linear in the specified temperature range. The luminescence intensity from the pressure sensor emission peak was found to be temperature independent. In addition, communications with Northrop Grumman during Phase I have lead to a partnership for independent testing of the sensor paint in a development wind tunnel.

The porphyrin-europium complex developed herein is unique in that simple modifications to the structure will allow for tuning the emission peak position and the lifetime of the excited states to within specifications of the end user. A proposed structure for modifications is shown in Figure 6-1. Two europium metals can be coordinated to the porphyrin ring by changing the reactant stoichiometry during porphyrin synthesis to incorporate two pyridine groups in the meso position. This would increase the intensity of the temperature sensor emission peak intensity to match that of the pressure sensor. In addition to further evaluation of europium-based temperature sensors, other lanthanide metals such as praseodymium, neodymium, terbium and erbium can be



M = 2H, Co(II), Pd(II), Pt(II), etc...

Ln = Eu(III), Pr(III), Nd(III), Tb(III), etc..

Figure 6-1. Structure of proposed modifications to Phase I sensor complex.

coordinated to the porphyrin ring. The change in lanthanide metal will influence the energy levels of the electronic state of the temperature sensor and result in a shift in emission energy and excited state lifetime. Another approach for optimizing the temperature and pressure sensitive compound is by the insertion of a metal in the porphyrin ring. Metals such as platinum, palladium, copper, and iron will be investigated. The effect of metal insertion is to shift the intense absorption band associated with the porphyrin resulting in a simple modulation of the porphyrin to give specific spectroscopic properties.

During continued development of sensor complexes, the bi-chromophoric sensor compound containing a ruthenium-based pressure sensor and a $Eu(TTA)_3$ temperature sensor will be revisited. Thus far, the synthetic procedure involving the combination of monometallic ruthenium complex with monometallic europium through a bipyrimidine bridging ligand was unsuccessful. In one trial, the bipyrimidine was successfully attached to the ruthenium complex but was unreactive toward the coordination of europium. It is now believed that these attempts failed in part due to the positive charge on the ruthenium complex which makes the bipyrimidine nitrogens less basic and therefore less reactive. By synthesizing the neutral ruthenium complex, shown in Figure 6-2, this problem should be remedied and will result in the creation of the first Ru(II)/Eu(III) bimetallic temperature and pressure sensitive compound.

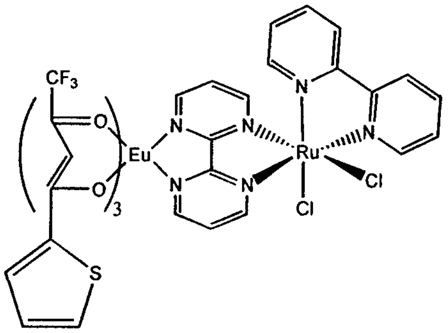


Figure 6-2. Proposed bi-chromophoric ruthenium-europium pressure and temperature sensor complex.

Other on-going work at NanoSonic will enable the synthesis of a more robust binder matrix for the sensor paint. The current state of the art for suspending temperature and pressure sensitive probes for spray application relies on the use of fluorinated polymethacrylates. These polymers offer the necessary oxygen permeability for the sensors in the resulting films. Despite their successful application, this matrix suffers from low thermal decomposition temperatures and poor mechanical properties. To extend the use of sensor paints for analysis of structures in high velocity environments, both of these issues must be addressed.

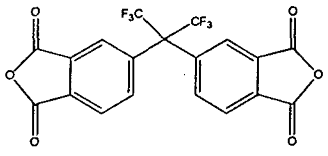
During the Phase II period, NanoSonic will investigate the use of fluorinated polyimides as thermo-oxidatively stable matrices for pressure and temperature-sensitive paints. Polyimides are well known engineering polymers due to their high thermal and oxidative stability and exceptional mechanical properties. These desirable properties have lead to their use in a variety of high performance applications such as films, electronics devices, and support matrices. The rigid, heterocyclic structure of polyimides affords high glass transition temperatures (Tg) up to 300°C, high modulus, and modest solvent resistance, depending on incorporated backbone functional groups.

Fluorinated polymers, in general, are noted for their chemical and temperature stability. These properties are attributed to a 'self-organizing' mechanism during which fluorine atoms migrate to the surface to create a fluorine-rich, high energy surface. The generated hydrophobic surface is resistant to wetting/nucleation by most contaminates (e.g., water, biological, etc.).

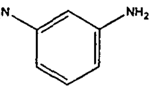
The proposed partially fluorinated polyimides will be synthesized in-house by NanoSonic. Polymerization follows a robust step-growth mechanism leading to well defined polymeric materials. The advantageous selection of monomeric precursors from a library of reagents, Figure 6-3, also allows us to tune the thermal, oxygen permeability, solution characteristics and mechanical properties of the resulting films. The performance of these matrices will be assessed versus the polymethacrylates currently in use.

The following is a list of tasks that would be pursued during a Phase II effort to commercialize a pressure and temperature-sensitive paint.

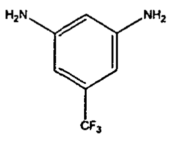
- Measurement of excited-state lifetimes of sensor chromophores.
- Re-formulate paints using an in-house fluorinated polyimide binder matrix.
- Analyze and calibrate paints containing temperature and pressure sensor compounds in the full pressure and temperature range.
- Modify bi-chromophoric compounds through iterative chemical processing to meet performance criterion.
- Up-scale production of prototype sensor coating material and deliver to Air Force and defense contractors for evaluation.
- Work with Northrop Grumman Aircraft Systems Division in El Segundo, CA through a small subcontract to experimentally evaluate methods for sensor coating application and performance in development wind tunnel systems.



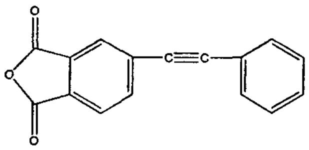
4,4'-Hexafluoroisopropylidenebis(phthalic anhydride) "6FDA"



1,3-Phenylenediamine "m-PDA"



3,5-diaminobenzotrifluoride "3,5-DABTF"



4-Phenylethynylphthalic "4-PEPA"

Figure 6-3. Monomeric precursors for the synthesis of high temperature stable polyimides.

6.1 Combination of Sensor Paints and Self-Assembled Coating Technology

During the Phase II program, we also envision attempting to combine the paint sensor coating materials and concepts developed during Phase I with existing self-assembly synthesis technology used by NanoSonic to fabricate other materials such as Metal Rubber™. Self-assembly is a coating process that NanoSonic has developed for the manufacturing of robust, conformal coatings on a variety of substrate surfaces, including full-scale aircraft canopy transparencies. It is based on the alternate adsorption of oppositely-charged molecular species onto a cleaned and functionalized substrate. NanoSonic's unique technology developments in this area have been 1) process improvements to allow the formation of uniformly dispersed coatings up to a millimeter in thickness, and 2) the incorporation of chemical release layers during processing to allow the formation of free-standing sheets of self-assembled material that may be used subsequently as appliqués on structural components. Here, this process could be modified to incorporate inorganic sensor materials into the coating or free-standing sheet stock material. The process itself could be used to entirely coat wind tunnel models, which would avoid potential problems associated with painting on sensor paint layers. Sensor appliqué materials could be used instead to conformally form highly flexible layers of material onto model surfaces, or the surfaces of full-scale flight vehicles.

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