

TECHNICAL NOTE

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A New Europium Chelate As a Fluorescent Dye for Cyanoacrylate Pretreated Fingerprints—EuTTAPhen: Europium ThenoylTrifluoro-Acetone Ortho-Phenanthroline

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ABSTRACT: The use of luminescent dyes to enhance fingerprints developed with cyanoacrylate is now a well established procedure in most fingerprint laboratories. Misner, Wilkinson and Watkin [1] have proposed a new fluorescent dye using an Europium complex (TEC). The purpose of the present paper is to report on further studies of this dye (TEC) and some analogues. Preliminary tests on cyanoacrylate pretreated fingerprints showed that a formulation of EuTTAPhen (Europium ThenoylTrifluoroAcetone ortho-phenanthroline) was the most efficient complex giving the best luminescence intensity of the treated fingerprints, a Stokes shift of 262 nm and reduced practical drawbacks.

KEYWORDS: criminalistic, fingerprints, cyanoacrylate, dyes, Europium, luminescence, EuTTAPhen

The use of luminescent dyes to enhance fingerprints developed with cyanoacrylate is now a well established procedure in most fingerprint laboratories. Many dyes, such as Rhodamine 6G, Ardrex or Basic Yellow 40, are readily available and frequently used in routine either to introduce contrast or to increase sensitivity of detection. Depending on the nature of the surface background may prevent good detection.

Misner, Wilkinson and Watkin [1] have proposed a new fluorescent dye using an Europium complex (TEC) which emits a narrow band (10–20 nm wide) at 614 nm when excited with UV light near 350 nm. The large Stokes Shift combined with a narrow emission band are the most sought out features. The purpose of the present paper is to report on further studies of this dye (TEC) and some analogues.

Preliminary results have shown that excessive background adheres to the treated surface with the proposed formulation and that the prints had to be thoroughly washed with the solution proposed (80% methanol, 15% water, 5% Tergitol) in order to

obtain a good contrast. Nevertheless, depending on the surfaces, this washing solution is inefficient and cannot remove the excess of the dye. This may be why Wilkinson & Watkin have proposed a 10-fold diluted formulation in their subsequent article [2], therefore reducing the background problem but the present study indicates that the luminescence intensity of the treated prints is then sensibly decreased.

These elements, added to some practical drawbacks such as the risk of washing off the prints with the methanol/water/Tergitol solution or the risk of not being able to remove the excessive background, led us to study new Europium complexes and to use them as powders dissolved in solvents based on petroleum ether (volatile 30–50°C fraction) [3].

Three Europium complexes were obtained from the Institute of Mineral and Analytical Chemistry (University of Lausanne) who had prepared them for their own research, and two other complexes were prepared following a simple procedure described by this research group (Bünzli and co-workers [4]). Preliminary tests on cyanoacrylate pretreated fingerprints showed that a formulation of EuTTAPhen (Europium ThenoylTrifluoroAcetone ortho-phenanthroline) was the most efficient complex giving the best luminescence intensity of the treated fingerprints, a Stokes shift of 262 nm and reduced practical drawbacks. Furthermore these compounds offer long luminescence signal (0.3 to 0.6 ms) that make them ideal for time resolved detection such as proposed by Menzel & Mitchell [5].

Material and Methods

Reagents

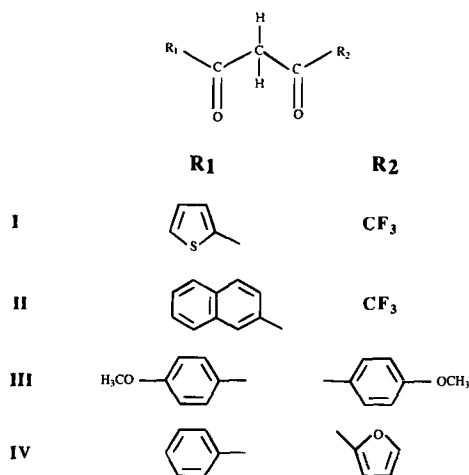
Of the five complexes studied, four are formed using β -diketones ligands (Fig. 1, I to IV) and one is formed using a terpyridine ligand.

Finally, the structure of the Europium chelate can be illustrated as follows (Figure 2):

Three molecules of β -diketone are needed for one atom of Europium and the molecule bound with the two nitrogen atoms is a molecule of ortho-phenanthroline which is added to increase the coordination number from 6 to 8, which has the effect of better protecting the chelate from solvent interactions. The chelates formed with the ligands I and II were prepared following the procedure described by Bünzli and co-workers [4].

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- I** R₁ is substituted by a thienyl group and the name of this ligand is 4,4,4 trifluoro-1-(2-thienyl)-1-3-butanedione (thenoyltrifluoroacetone) and is the ligand used by Wilkinson and Watkin.
- II** R₁ is substituted by a naphthyl group instead of a thienyl group and the name of this ligand is 4,4,4 trifluoro-1-(2-naphthyl)-1-3-butanedione (naphthyltrifluoroacetone).
- III** R₁ and R₂ are each substituted by a methoxyphenyl group.
- IV** R₁ is substituted by a phenyl group and R₂ is substituted by a furyl group.

FIG. 1—Structures of β -diketone ligands.

The two chelates using the ligands I and II were prepared as follows:

Note that all the chemicals are analytical grade and furnished by Fluka, Switzerland.

- 67 mg of thenoyltrifluoroacetone (80 mg for naphthyltrifluoroacetone) and 20 mg of ortho-phenanthroline are dissolved in 100 mL of ethanol (Solution 1).

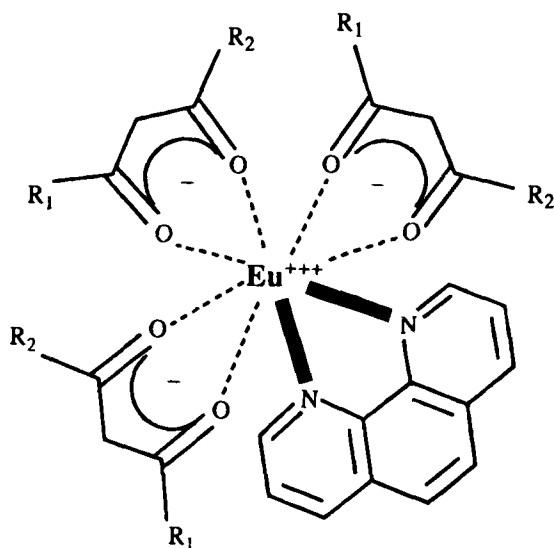


FIG. 2—Structure of a Europium complex when bound with 3 molecules of β -diketones ligands and one molecule of ortho-phenanthroline.

- 37 mg of Europium chloride hexahydrate are dissolved in 100 mL of ethanol and this solution is slowly added to the first one.
- The pH is adjusted to 6 by adding dropwise ethanolamine or triethylamine ($\sim 30 \mu\text{L}$).
- The solution is then evaporated under vacuo with the Rotavapor apparatus.
- The residue obtained is dissolved in a small quantity of acetone which is then poured in large crystallizing dishes. Acetone slowly evaporates at room temperature and residues crystallizes in the dishes.
- The crystallizing dishes are left for about 24 h in a desiccator in order to dry.
- These are then scraped with a spatula and a dusty pink powder of the Europium chelate is obtained.

The chelates formed with the ligands III and IV were obtained from the institute of Mineral and Analytical Chemistry (University of Lausanne). In the case of the chelate formed with the ligand IV, two molecules of triphenylphosphine oxide (TPPO, Fig. 3) were added instead of one molecule of ortho-phenanthroline, the two compounds having exactly the same purpose, each molecule of TPPO being bound to the Europium by its oxygen atom while the ortho-phenanthroline is bound to the Europium by its two nitrogen atoms.

The fifth chelate was also obtained from the same Institute and instead of a β -diketone ligand uses a terpyridine ligand (three molecules for one atom of Europium). The chelate is represented by the Fig. 4.

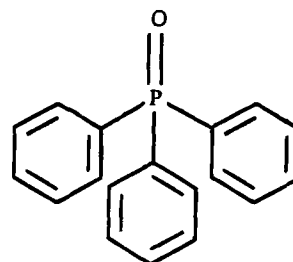


FIG. 3—Structure of a molecule of triphenylphosphine oxide.

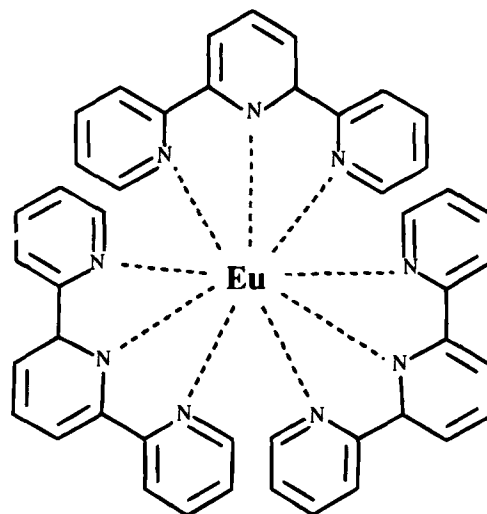


FIG. 4—Structure of a Europium complex when bound to three molecules of terpyridine.

Variable quantities of these five chelates, 0.01 to 0.05 g, were dissolved in propanol (3 mL) and acetonitrile (2 mL) to form stock solutions. Then 0.5 mL of the stock solutions were diluted with petroleum ether (volatile 30–50°C fraction) to 10 mL to form working solutions.

General

Luminescence examinations were conducted using excitation from a tuneable light source (Polilight PL10, Rofin, Australia) with observation of the emission using an appropriate interference filter.

Photographs were taken with an Olympus OM4 Ti, using the following conditions:

Film: Kodak Ektakrom 64T
Diaphragm: 4.5
Exposition time: about 3 minutes

Excitation and emission spectra were measured directly on a treated fingerprint (on a glass object-slide) using a LS 50 spectrofluorimeter (Perkin Elmer).

Preliminary tests on cyanoacrylate pretreated fingerprints (fresh prints on white, black and multicolored polyethylene shopping bags) were carried out with the working solutions described above in order to determine the most efficient formulation.

These showed that the formulation with Europium Thenoyl-TrifluoroAcetone ortho-phenanthroline, "EuTTAPhen" as named by Li, Yu and Zhao [6] gave the best luminescence intensity of the treated fingerprints.

The final formulation was determined according to two criteria: the background noise and the luminescence intensity. With these criteria, the optimum formulation was found to be the following

EuTTAPhen formulation

Stock solution: EuTTAPhen (0.5 g) dissolved in propanol (60 mL) and acetonitrile 40 mL).

Working solution: the stock solution (5 mL) diluted with petroleum ether (to 100 mL).

This formulation was then tested by comparison with TEC [2] on prints cut in a half.

In addition the EuTTAPhen dye could easily be mixed with other common cyanoacrylate stains, such Rhodamine 6G or Basic Yellow 40.

EuTTAPhen + Basic Yellow 40 formulation

Stock solution: Basic Yellow 40 (0.1 g) dissolved in propanol (60 mL) and acetonitrile 40 mL).

Working solution: EuTTAPhen stock solution (2 mL) is mixed with Basic Yellow 40 stock solution (3 mL) then diluted with petroleum ether (to 100 mL).

Fingerprints on various surfaces (for example, a coke can, a phonocard, plastics, metal or white porcelain) were developed by conventional cyanoacrylate fuming. These prints were subsequently treated in each case by application of the staining solution with a pipette.

Results

The excitation and emission spectra are illustrated in Figs. 5 and 6. One can see that there is a broad excitation band (310 to 390 nm) with a maximum at about 350 nm and a narrow 20 nm wide emission band with a peak at 612 nm, which gives a very important Stokes shift of 262 nm.

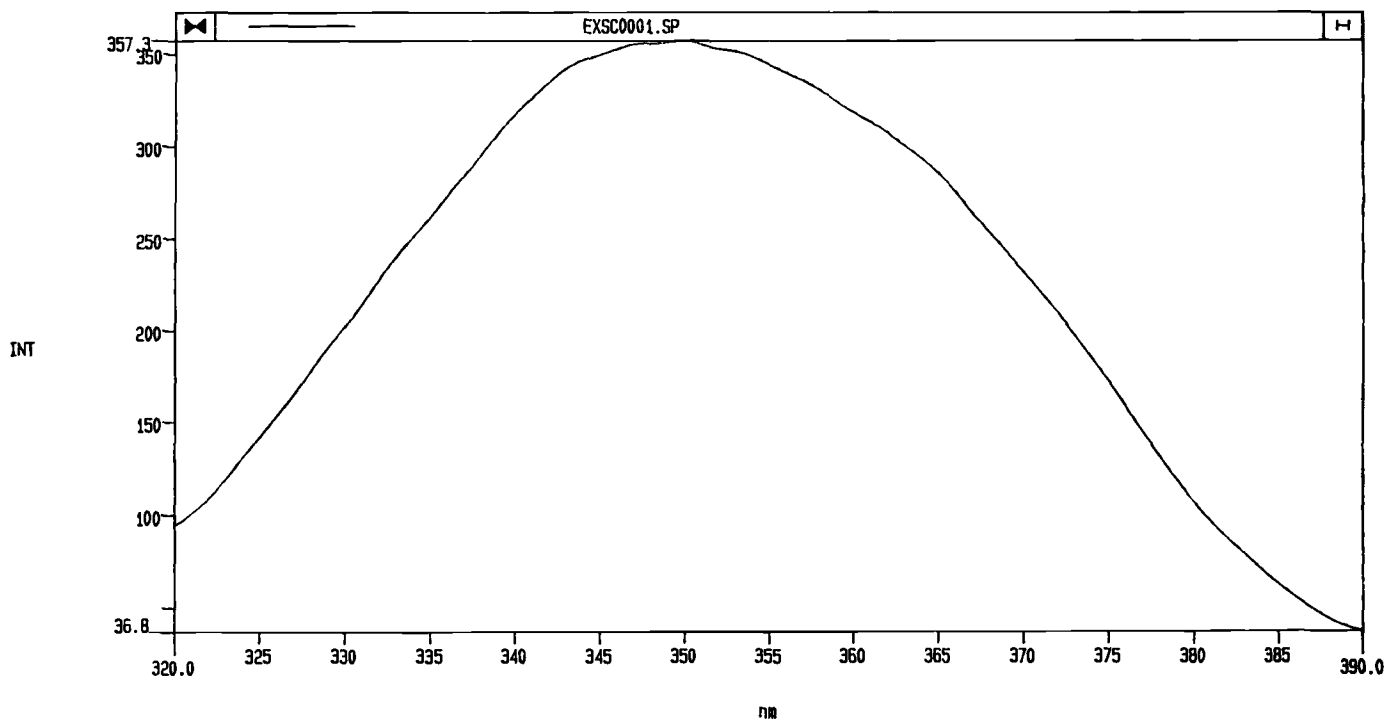


FIG. 5—The excitation spectrum of EuTTAPhen.

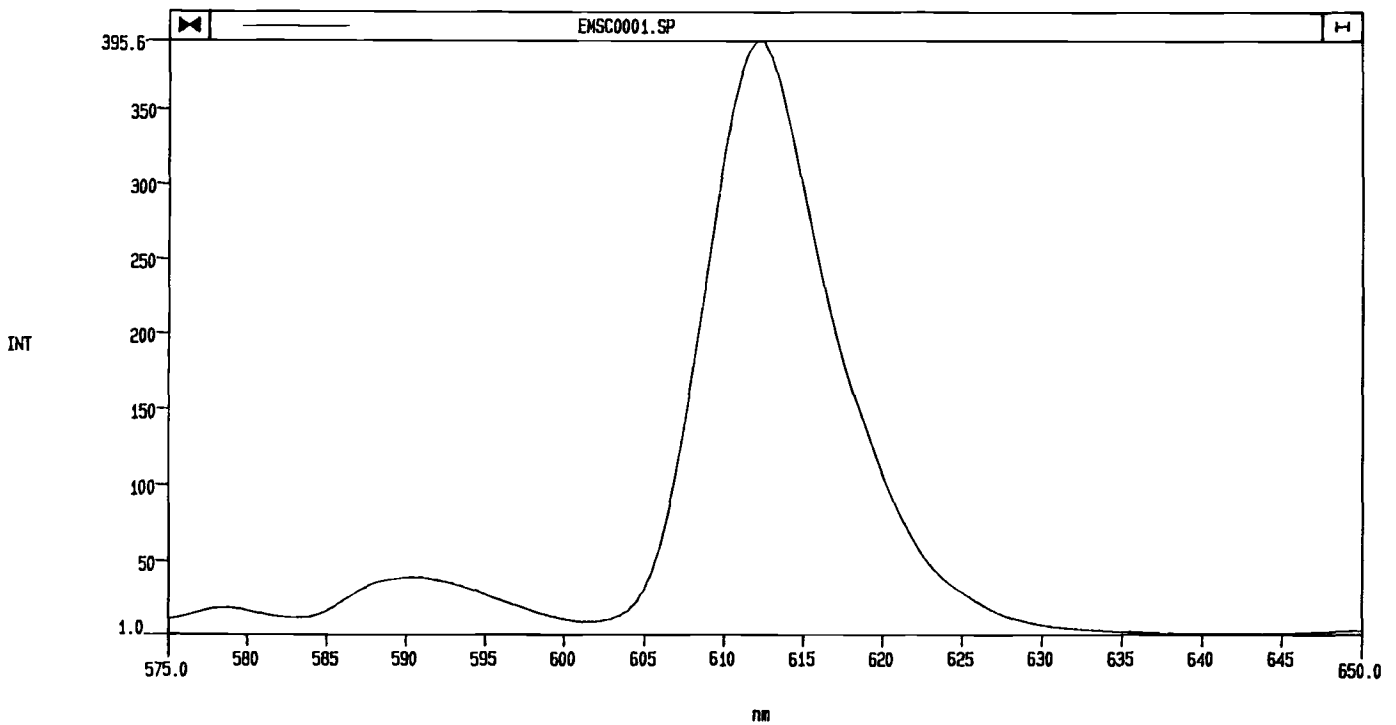


FIG. 6—The emission spectrum of EuTTAPhen.

The results obtained with the EuTTAPhen working solution on various non-porous surfaces are summarized in the Table 1.

Figure 7 show the staining with EuTTAPhen of a latent print developed with cyanoacrylate on a multicolored credit card.

The EuTTAPhen formulation shows a higher luminescence intensity, see for example Fig. 8, and generally less background problems compared to the TEC [2] (nevertheless sometimes, depending on the surfaces, the background noise could be higher).

The mixed solution (EuTTAPhen + Basic Yellow 40) gave interesting results. Fingerprints treated with this solution showed emission bands at 550 nm and 610–615 nm when radiated at 450 nm and 350 nm respectively. In addition the solution presented an emission band at 550 nm when excited at 350 nm. The mixed solution extends the range of wavenlengths available with a single



FIG. 7—Cyanoacrylate print developed on a multicolored plastic credit card dyed by EuTTAPhen.

TABLE 1—Results of the EuTTAPhen formulation on various non-porous surfaces.

Surfaces	Good	Satisfactory	Poor
White plastic	X		
Colorless plastic	X		
Colored plastic	X		
Black Plastic	X		
Caoutchouc type	X		
Glass		X	
Aluminum foil	X		
Aluminum can, Red surface		X	
Porcelain	X		
Metal	X		
Credit card	X		
Plastified cardboard	X		
Postcard		X	
Brilliant paper		X	
Magazine Paper			X



FIG. 8—Cyanoacrylate print developed on a colorless plastic dyed by TEC (left side) and EuTTAPhen (right side).

dye mixture; this could be an advantage when working with some difficult surfaces.

Conclusion

EuTTAPhen is a new fluorescent dye for cyanoacrylate pre-treated fingerprints which is the outcome of further studies on Europium complexes and especially of the dye proposed by Misner, Wilkinson and Watkin (TEC).

This new dye has the same spectral properties as the TEC but a higher luminescence intensity makes it polyvalent and efficient on many surfaces. The formulation is based on petroleum ether instead of methyl ethyl ketone and water. Petroleum ether was chosen for its low cost, availability, low toxicity, low polarity and high volatility. In addition, the EuTTAPhen dye could easily be mixed with other common cyanoacrylate stains, such Rhodamine 6G or Basic Yellow 40.

The good results observed on many surfaces and the low background noise make the EuTTAPhen formulation very attractive.

Acknowledgments

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