

Colorless Crystals of Tautomeric Fluoran Indicator Dyes

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Abstract

Some indicator dyes can exist as either a colorless or a colored tautomer, depending upon the environment. We have found examples of fluoran dyes (fluorescein, rhodol, and rhodamine) for which there exist crystalline forms of the colorless tautomer, but which in other crystalline habits or in the glassy state exhibit substantial absorption in the visible. The melting of colorless particles of these dyes provides a mechanism for direct thermal imaging characterized by high sensitivity for a given level of stability. The optimization of these amorphochromic dyes for direct thermal imaging will be described.

Introduction

Thermally sensitive recording paper was pioneered by National Cash Register in 1968 and is a ubiquitous product today.¹ Colorless crystals of a leuco dye and one or more color-forming coreactants are coated together as separate crystalline phases. When either or both of the materials are melted they diffuse together to produce a wide array of colors. By far the preferred color for thermal recording paper is black. Recently, thermal recording papers using two or more different color forming layers have been developed. Fuji's Thermo-Autochrome uses a cyan leuco dye in combination with a zinc salicylate to produce a cyan image. This is done in combination with separately addressable yellow and magenta images produced by diazonium coupling reactions. Photographic quality images are produced by this process. Thermally sensitive media which depend on diffusion are difficult to stabilize. To get sensitivity, at least one of the melting points must be low. However, stability is governed by the melting point of the eutectic that forms at the interface of the crystalline phases when the ingredients diffuse together when exposed to a stressful environment of heat and/or humidity. If either of the components recrystallizes or diffuses apart the image fades. In this talk we will discuss fluoran molecules which are colorless in the crystalline state, but when melted directly form a highly colored amorphous state without the need for a color promoting co-reactant. We have discovered many examples of each of the three subtractive primary colors in which a substantially colorless crystalline form melts at temperatures ranging from 80-310 C to produce highly colored amorphous melts in a unimolecular color-forming process (Figure 1). Monochrome images with low minimum densities and highly saturated maximum densities can be produced using the fluoran dyes described in this paper.

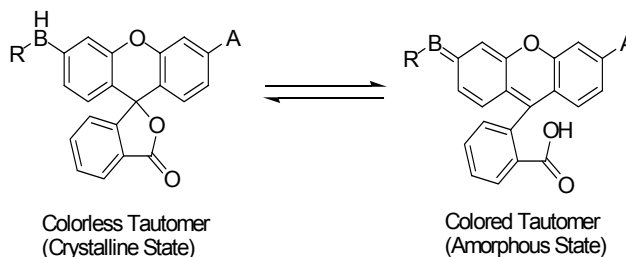


Figure 1. Fluoran tautomerization between colorless and colored states.

Yellow Amorphochromic Fluorans

We started searching for fluorans with a white crystalline form which melted to a colored amorphous form. We developed a simple screening test. Substantially colorless crystalline fluorans were dissolved in a non-polar solvent at a concentration of 1-2% and then coated as a thin film of the amorphous colored form with a Mayer rod. Materials which are 20-50% in the colored tautomer in this test are candidates for imaging systems. We soon discovered that fluorescein ethers have this property. However, the equilibrium of the simple fluorescein ether **1** strongly favored the colorless form (96%). Nevertheless, we were able to clearly demonstrate the viability of the concept and embarked on a synthetic program to find improved materials. Initially, we tried electron-withdrawing groups in the 4,5,6,7 positions of the phthalide ring with little success. However, adding electron-rich substituents to the xanthene moiety stabilized the open colored form and improved the equilibrium. Addition of alkyl groups in the 3',6' positions had a remarkable effect on the equilibrium of fluorescein ethers with approximately 30% coloration in the amorphous state while still having a colorless crystalline form. The alkyl groups also provided a method to adjust the melting point and other physical properties such as T_g and water solubility. Table 1 summarizes a number of amorphochromic yellow fluorescein ethers.²

Magenta Amorphochromic Fluorans

Two approaches were pursued to find magenta amorphochromic dyes and both proved viable. Rhodols and rhodamines both proved to be sources of amorphochromic magenta chromophores. Whereas, yellow amorphochromic dyes were discovered quickly, magenta provided additional challenges. Rhodols traditionally are more red than magenta and the equilibrium strongly favored the colored tautomer. Unlike the fluorescein ethers it was very difficult to find colorless rhodol crystals which had the requisite imaging properties. We discovered that rhodols often crystallized as colorless complexes with hydrogen bond acceptors **A** such as pyridines, imidazoles and amides. The melting point of the complex could be adjusted by changing the complexing agent or

adjusting substituents on the rhodol. We were also able to bathochromically shift the rhodol chromophore from red to magenta through the incorporation of halogens in the 4,5,6,7 positions of the phthalide ring. Table 2 summarizes a number of amorphochromic red and magenta rhodol complexes.^{3,4} Table 3 summarizes a number of amorphochromic magenta rhodamines.

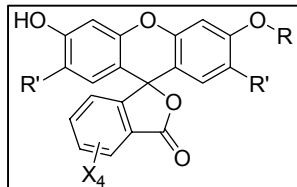


Table 1: Examples of Yellow Amorphochromic Fluorans

Dye	R'	R	X	mp
1	H	CH ₂ C ₆ H ₅	H	165
2	H	CH ₂ C ₆ H ₅	4,5,6,7-Cl ₄	284
3	H	CH ₂ C ₆ H ₅	5-NO ₂	137
4	C ₂ H ₅	CH ₂ C ₆ H ₅	H	222
5	C ₃ H ₇	CH ₂ C ₆ H ₅	H	208
6	C ₆ H ₁₁	C ₂ H ₅	H	125
7	C ₆ H ₁₁	CH ₃	H	132
8	C ₄ H ₉	C ₂ H ₅	H	158
9	C ₅ H ₁₁	C ₂ H ₅	H	150

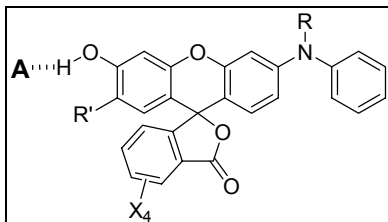


Table 2: Examples of Magenta Amorphochromic Rhodol Complexes with Hydrogen Bond Acceptors

Dye	Hydrogen Bond Acceptor: A	Ratio A:Rhodol	R'	R	X ₄	m.p.
10	4,4'-Bipyridyl	1:2	Br	C ₁₆ H ₃₃	H	80
11	4,4'-Bipyridyl	1:2	Br	C ₁₂ H ₂₅	H	107
12	4,4'-Bipyridyl	1:2	Br	C ₁₀ H ₂₁	H	125
13	4,4'-Bipyridyl	1:2	Br	C ₆ H ₁₁	H	155
14	4,4'-Bipyridyl	1:2	Br	C ₂ H ₅	H	210
15	4,4'-Bipyridyl	1:2	C ₆ H ₁₁	i-C ₅ H ₁₁	Cl	180
16	4,4'-Bipyridyl	1:2	C ₆ H ₁₁	C ₆ H ₁₁	Cl	140
17	N-Acetyl indoline	1:1	C ₆ H ₁₁	i-C ₅ H ₁₁	Cl	139
18	1-Benzyl imidazole	1:1	C ₆ H ₁₁	i-C ₅ H ₁₁	Cl	133

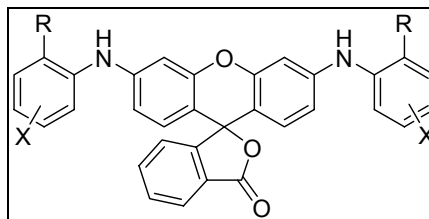


Table 3: Examples of Magenta Amorphochromic Rhodamine Dyes

Dye	R	X	m.p.
19	H	H	270
20	CH ₃	H	173
21	i-C ₃ H ₇	H	165
22	CH ₃	5-i-C ₃ H ₇	137
23	CH ₃	4-CH ₃	175

Cyan Amorphochromic Fluorans

Developing a cyan amorphochromic fluoran was our biggest challenge. Our experience in fluoran dyes suggested we could bathochromically shift a rhodamine dye to cyan. We quickly proved with a mono-indoline, mono-aniline substituted fluoran that we could move beyond 600 nm. Incorporation of chlorines in the 4,5,6,7 positions of the phthalide provided us with amorphochromic cyan dyes of a wide range of melting points. However, these dyes were highly thermochromic. When printed with a thermal printhead, the initial densities were quite low. The dye would then cool quickly and lock in the poor equilibrium. This would then change dramatically over hours or days as the dye would relax to its true equilibrium upon accelerated aging. A solution to this problem was found by replacing the bulky chlorine substituents with fluorines. Although the tetrafluorofluorans were also thermochromic, they readily achieved their true equilibrium in imaging media and provided viable cyan color formers. Table 4 summarizes a number of cyan amorphochromic color formers.⁵

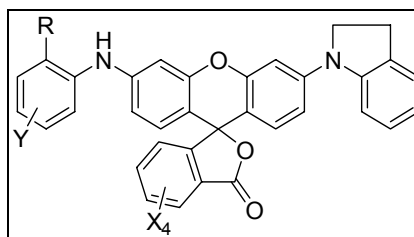


Table 4: Examples of Cyan Amorphochromic Fluoran Dyes

Dye	R	Y	X ₄	m.p.
24	H	3,4-bisOC ₈ H ₁₇	Cl ₄	130
25	H	3,4-bisOCH ₃	Cl ₄	160
26	CH ₃	4-OCH ₃	F ₄	210
27	CH ₃	4-OC ₁₀ H ₂₁	F ₄	142
28	CH ₃	4-OC ₁₂ H ₂₅	F ₄	139
29	CH ₃	4-OC ₁₄ H ₂₉	F ₄	136
30	CH ₃	4-OC ₁₈ H ₃₇	F ₄	129
31	CH ₃	4-F	F ₄	204
32	CH ₃	CH ₃	F ₄	218

Summary

This paper demonstrates novel fluoran structures. These fluorans possess a colorless crystalline form and melt to produce a highly colored amorphous form. These amorphochromic fluorans have potential utility as unimolecular color formers for thermal printing papers. When fully optimized these materials have the potential of producing high quality yellow, magenta and cyan images of high sensitivity and high stability.

References

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Author Biography

Michael P. Filosa is currently a Senior Manager of Science and Technology at the Polaroid Corporation. He received his bachelor's degree in chemistry from the Massachusetts Institute of Technology in 1974 and his Ph.D. degree in Organic Chemistry at Harvard University in 1979. Since 1979 Michael and his research group have supported Polaroid product development with novel imaging chemicals including amorphochromic cyan, magenta and yellow dyes for photographic quality direct thermal imaging.