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Color intensity control in polymers using triarylmethane leuconitriles as color formers☆

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Abstract—Several triarylmethane leuconitriles have been synthesized. Color formation rates of triarylmethane dyes from corresponding leuconitriles have been compared in various media. Routes to color-on-demand processes are discussed.

1. Introduction

The color formation properties of triarylmethane leuconitriles have been studied for years.[1] This paper describes the controlled color formation from triarylmethane leuconitriles in photochemically cured polymers, including cationically cured systems. The routes for controlling the rate of color formation are discussed. New leuconitriles have been synthesized and analyzed as color formers.

In general, the majority of species used to irreversibly form color on demand in solution or in polymeric matrices contains functional groups sensitive to the concentration of the protons in the medium. Since most photocurable cationic monomer systems require instantaneous formation of protons to cure the resin, these simultaneous color formation processes become uncontrollable in such systems. As a result, non-acid-sensitive color formers are required, and tri- and diarylmethane color formers (TAM-X and DAM-X) that undergo unimolecular photoassisted dissociation (X=CN, hydrocarbon, SO_3H) are especially important for the polymeric systems that cure via a cationic mechanism.

The use of dyes that produce color via unimolecular dissociation reactions allows one to avoid nonpropitious routes to color formation such as those caused by acid/base indicator action. We have shown that in epoxide resins the rate of color formation is practically independent of the photoacid generator concentration. In fact, the color formation rate is slightly higher when the photoacid generator is removed from the epoxide resin entirely.

Several leuconitriles have been synthesized and tested as color formers in epoxide resins. Dye concentration was varied, and in most cases, 0.05% of the dye is enough to obtain strongly colored objects. Varying the dye concentration or/and changing the irradiation dose applied to the cured resin controls the resulting color intensity. By changing the anionic leaving group and the substituents on the phenyl ring of triarylmethane leucodyes, it is possible to either enhance or retard the rate of the color formation. The choice and position of the substituent(s) on the phenyl ring also allow one to tune the maximum absorption wavelength (color) of the photocured polymer.

Color on demand is a developing technology in which a photocurable monomer is scanned by a computer-driven laser, or other digital light source, to form a solid object with a distinct shape. Our group has been interested in extending this technology for some time, and one of our objectives has been to control color formation in polymeric systems using photochemistry.[2,3] Such systems, if developed, could be applied in various applications, making it possible to form two- and three-dimensional objects having certain areas distinctly colored and in sharp contrast to the rest of the object. In other words, we want to develop a system in which a colorless dye dissolved in a monomer or oligomer is scanned by a light source, forming colorless polymer. The polymer could then be rescanned in an imagewise fashion, using light of a different intensity and/or wavelength, to activate the dye and form color in specific areas.

Dyes based on Malachite Green (**1A**) have been among the

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Keywords: triarylmethane leuconitrile; photoactive dye; color formation; photopolymerization; epoxide.

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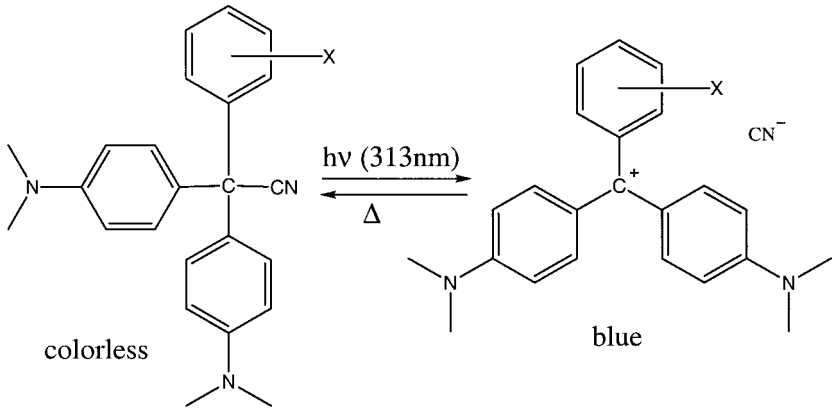


1A X = H
2A X = 2-fluoro
3A X = 3-fluoro
4A X = 4-fluoro
5A X = pentafluoro

1B X = H
2B X = 2-fluoro
3B X = 3-fluoro
4B X = 4-fluoro
5B X = pentafluoro

Scheme 1. Irradiation of the leuconitriles.

most important types of color formers for over 100 years, and date to Fischer's original synthesis of the parent structure in 1877.[4] The strong color produced by such compounds would be desirable in the aforementioned color-on-demand systems to obtain a better contrast in the imaging system. It is also known that the corresponding leuconitriles of such dyes undergo heterolytic cleavage of the cyanide moiety upon irradiation with UV light, forming the colored cation[5–8] (Scheme 1).

We reasoned that if the resulting cation could be destabilized relative to the parent triarylmethyl carbenium ion, we might be able to slow down the cleavage of the cyanide, and hence slow down the rate of color formation. The introduction of a fluorine atom on the phenyl ring of Malachite Green would give the desired electronic effects. The introduction of fluorine into the triarylmethane structure is known.[9,10] However, the synthesis of the corresponding leuconitriles has not been reported. Therefore, we designed, synthesized and studied the photochemistry of such compounds in both solution and polymeric systems.

2. Synthesis

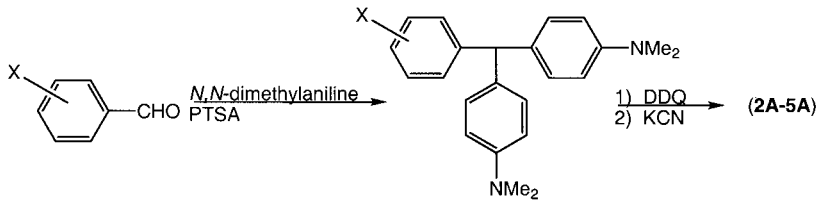
The synthesis of the fluorinated leuconitriles is shown in Scheme 2. *N*,*N*-dimethylaniline was condensed with the appropriate aldehyde (**2C**–**5C**) under acidic conditions to form the corresponding triarylmethane (**2D**–**5D**). The leucobases (**2D**–**5D**) were then oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to form the cations, which were quenched with potassium cyanide to form the leuconitriles (**2A**–**5A**).

The indole leucobase (**10D**) was synthesized from the corresponding benzhydrol and 2-methylindole (Scheme 3). Alkylation of **10D** was achieved using butyl lithium and butyl iodide to form **11D**. Compounds **10D** and **11D** were then oxidized and quenched with potassium cyanide to form the corresponding leuconitriles.

The other leuconitriles were synthesized via a metathesis reaction using the commercial dye and potassium cyanide.

3. Color formation in solution

Fluorinated triarylmethane leuconitriles were found to give highly colored solutions when irradiated in polar protic solvents such as methanol. However, in polar aprotic solvents such as tetrahydrofuran, little color was achieved after the leuconitriles were subjected to UV light. This is not entirely surprising as triarylmethanes are known to photoionize more rapidly in solvents with high dielectric



(**2C-5C**)

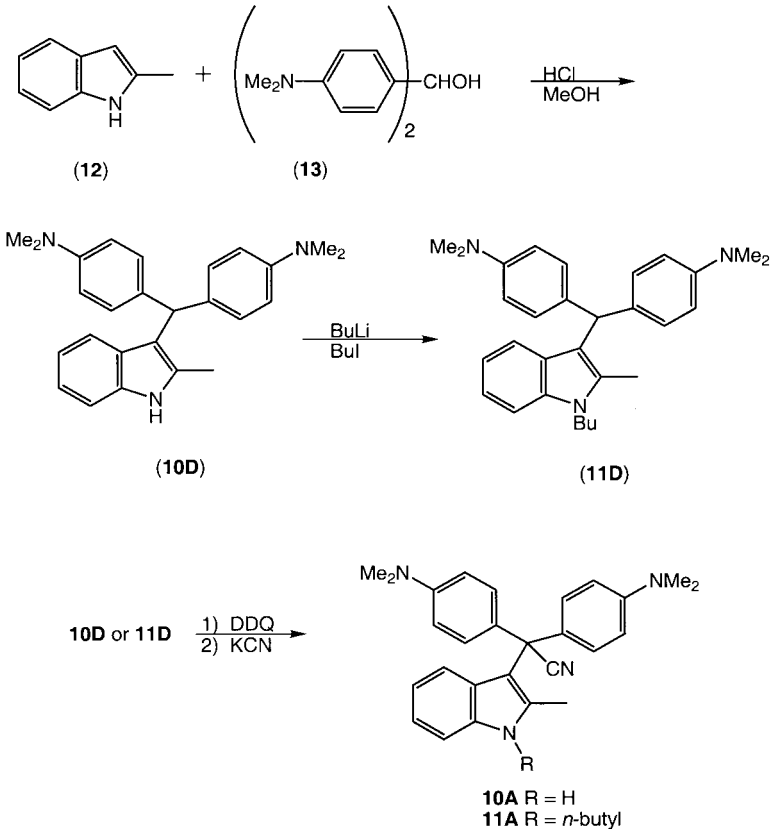
2C X = 2-fluoro
3C X = 3-fluoro
4C X = 4-fluoro
5C X = pentafluoro

(**2D-5D**)

2D X = 2-fluoro
3D X = 3-fluoro
4D X = 4-fluoro
5D X = pentafluoro

2A X = 2-fluoro
3A X = 3-fluoro
4A X = 4-fluoro
5A X = pentafluoro

Scheme 2. Synthesis of the fluorinated leuconitriles.



Scheme 3. Synthesis of the indole derivatives.

constants.[7] The pentafluoro compound (**5A**) achieved coloration most slowly, as can be seen from the rates of color formation in Table 1, and it also possesses the most red-shifted absorption maximum. The other dyes studied (compounds **2A**–**4A**) formed color almost immediately.

As can be seen from the UV spectrum in Fig. 1, the absorption at 656 nm steadily increases over time as does a minor peak at 424 nm. This spectrum was compared to the spectrum of the cation of Malachite Green. The two peaks can be assigned to the S_1 and S_2 transition. Moreover, the spectral shape obtained after several irradiation cycles agrees well with the spectrum of Malachite Green, and excitation of the samples at their absorption maximum (see Table 1) yielded an emission spectrum that mirrored the absorption spectrum. We assign this fluorescence to the emission of the colored product that is measurable in glassy materials.[11] Also of note is the slight increase of absorbance in the region $<$350 nm, signifying the formation of side products that interfere with the absorbance of light by the leuconitrile dye at prolonged irradiation times.

The pentafluoro cation (**5B**) formed after irradiation was found to be much more thermally stable than the rest after several irradiation cycles. The other dyes (**2B**–**4B**) began to bleach, losing the blue color, once they were placed in the dark (Table 1). This reaction occurs with first-order kinetics. The 2-fluoro derivative (**2B**) lost half of its original absorbance ($t_{1/2}$) in 402 min, while the 3-fluoro (**3B**) and the 4-fluoro (**4B**) compounds bleached even faster ($t_{1/2}$= 8.4 min for both compounds). The slower bleaching of the pentafluoro compound (**5B**) and the 2-fluoro compound (**2B**) is probably due to the *ortho*-substituted fluorines located on the adjacent aryl ring. These substituents crowd the neighboring methine carbon and prevent attack of nucleophiles that would quench the carbocation.

4. Color formation in PMMA films

The rate of color formation is much slower in the PMMA than in methanol, probably due to the nonpolar nature of the polymer matrix and the glassy nature of the material. Solvation of the carbocation formed under such conditions occurs more slowly than in ordinary organic polar solvents. Therefore, decoloration (back formation of the leuconitrile)

Table 1. Absorbance maxima λ (nm), inverse rate constants for thermal bleaching t (min) and color formation rate (apparative constant min^{-1}) for the compounds (**2A**–**5A**) in methanol and PMMA

No.	λ_{max} (MeOH)	λ_{max} (PMMA)	t (MeOH)	Color rate (MeOH)	Color rate (PMMA)
2	630	638	402	—	0.020
3	626	626	8.4	1.95	0.019
4	618	626	8.4	2.04	0.009
5	656	664	—	0.05	0.0013

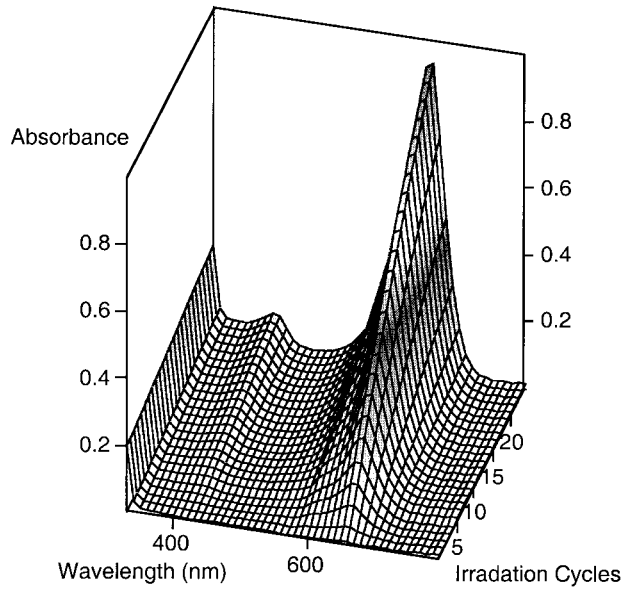


Figure 1. Irradiation of the pentafluoro leuconitrile (**5A**) in MeOH.

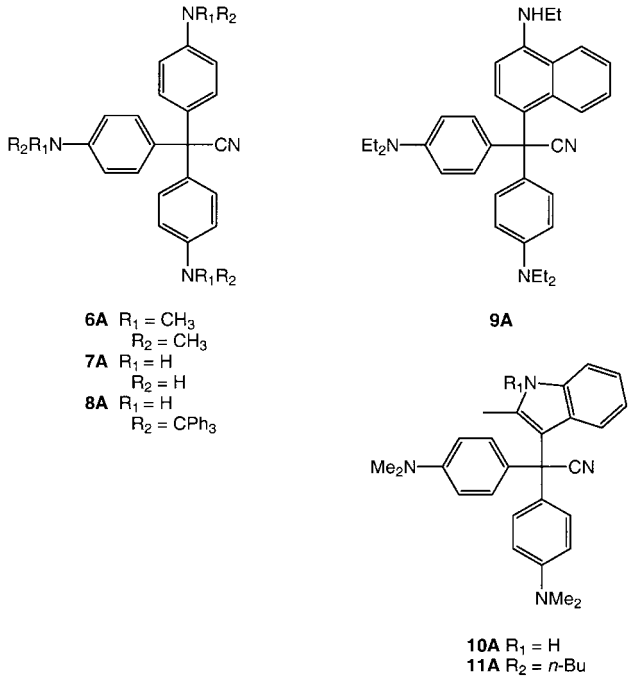


Figure 3. Structures of various leuconitriles.

can compete with photoionization (color formation). In addition the pentafluoro compound (**5A**) still forms color most slowly (Table 1). Unfortunately, the formation of byproducts after photolysis is much greater in the PMMA films (Fig. 2). These unwanted photoproducts produce a yellow color that, when combined with the blue color produced by the desired carbocation, forms an overall green color.

5. Color formation in epoxy resins

The method described in this work leads to controlled color formation in photochemically or thermally cured polymers. Triarylmethane dyes that undergo unimolecular photo-assisted dissociation are especially important for polymeric systems that cure via a cationic mechanism. The use of the triarylmethane dyes that produce color via unimolecular dissociation allows one to form color on demand, i.e. selectively.

Several triarylmethane leuconitriles have been synthesized

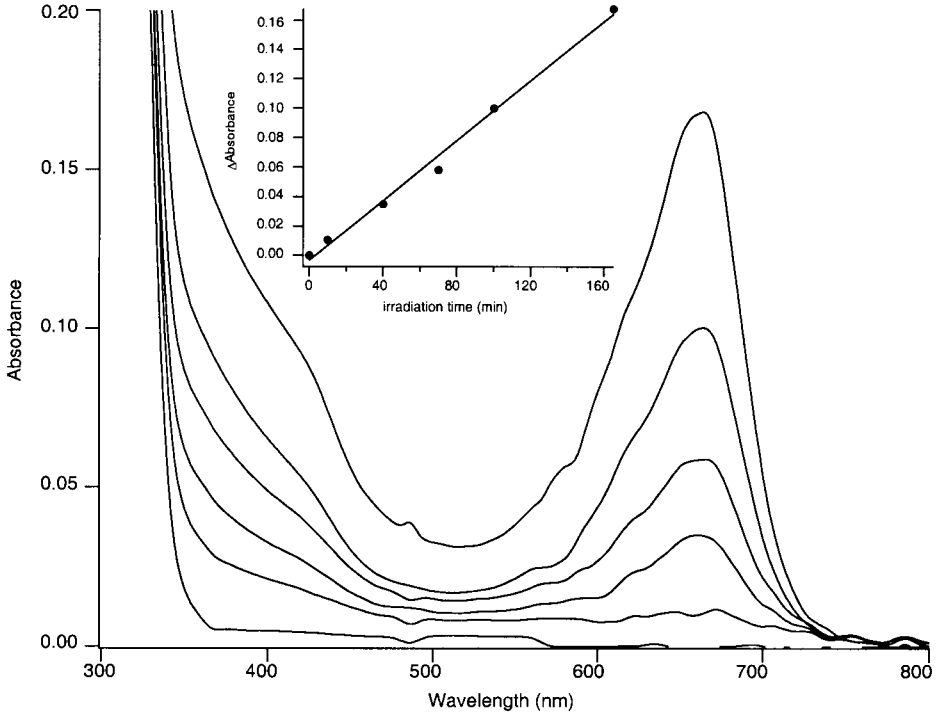


Figure 2. Irradiation of the pentafluoro leuconitrile (**5A**) in PMMA.

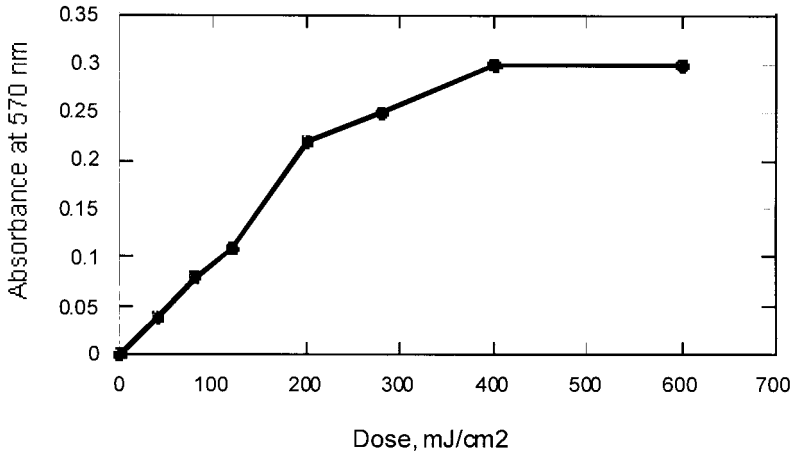


Figure 4. Color formation curve of **7A** (0.05 wt%) UVR-6110 containing 0.75% UVI-6974.

and tested as color formers in the hybrid system. By changing the anionic leaving group and the substituents on the phenyl ring of triarylmethane leucodyes, it is possible to enhance or retard the rate of the color formation. The choice and position of the substituent(s) on the phenyl ring also allow one to tune the maximum absorption wavelength (color) of the photocured polymer.

The leuconitriles that were tested (Fig. 3) were Malachite Green leuconitriles (**1A**, **2A**, **5A**), Crystal Violet leuconitrile (**6A**), Basic Fuchsin leuconitrile (**7A**), *N*-trityl protected Basic Fuchsin leuconitrile (**8A**), Victoria Pure Blue leuconitrile (**9A**), bis(4-dimethylaminophenyl)-(2-methylindol-3-yl) acetonitrile (**10A**), and bis(4-dimethylaminophenyl)-(1-butyl-2-methylindol-3-yl) acetonitrile (**11A**).

Each of these dyes was readily soluble in both acrylate and epoxide resins in small concentrations (<0.25 wt%). They also withstand temperatures up to 130°C with no detectable decomposition. The resin remains colorless upon the dissolution of these dyes.

As expected **5A** formed color most slowly upon irradiation. Compounds **7A** and **9A** produced the strongest color, and the color formation curve (Fig. 4) is not steep thus allowing one to obtain the desired color intensity by changing the exposure dose of the curing beam. By changing the leuconitrile, its concentration in the matrix, and the beam intensity one could obtain objects of different color and color brightness. It has to be noted that although leuconitriles are known for their photochromic properties, the cations that form do not bleach significantly in the cured epoxide resins in dark or in roomlight. Colors last for a period of at least 30 days. The results for different dyes are summarized in Table 2.

Table 2. Properties of 100 micron epoxide resin layer cured on a glass slide with a 325 nm laser beam (0.05 wt% dye and 0.75% UVI-6974 in UVR-6110)

Compound	Color	Max. abs. λ	Max. absorbance after 600 mJ cm^{-2}
1A	green	630	0.07
2A	green	640	0.07
5A	green	670	0.01
6A	blue	590	0.19
7A	purple	570	0.30
8A	purple	580	0.02
9A	blue	610	0.33
10A	purple	580	0.08
11A	purple	590	0.09

6. Conclusions

Several triarylmethane leuconitriles have been synthesized and characterized. Color formation of triarylmethane dyes from the corresponding leuconitriles has been studied in solution and in epoxide resins. It has been shown that various electron withdrawing and electron donating groups in the aryl functions of the leucodye influence the color formation rates in the media that were studied. By controlling the rate of color formation one may create a color-on-demand system with the color appearing after the sample has been exposed to a certain dose of irradiation of the chosen wavelength. Slow color formation rates prevent any significant color formation before other processes (such as polymerization) are complete. Subsequently, the color formation step becomes optional and can be carried out in the specified areas only.

7. Experimental

All starting materials and solvents were purchased from Aldrich and used without further purification. Flash column chromatography was performed on silica gel (Aldrich, 70–270 mesh, 60 Å) or aluminum oxide (Aldrich, activated neutral Brockman I, 150 mesh, 58 Å). Thin layer chromatography was performed on silica gel using glass-backed plates purchased from Aldrich (layer thickness 250 mm, particle size 5–17 mm, 60 Å) or on aluminum oxide plates (Aldrich, layer thickness 200 mm, particle size <60 mm, pore size 60 Å).

7.1. Measurements

NMR spectra were taken with a Varian Gemini 200 NMR spectrometer. GC/MS were taken on a Hewlett–Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m×0.25 mm ID×0.25 mm film thickness DB-5 ms column (J & B Scientific), interfaced to an HP 2623A data processor. UV–visible spectra were obtained using an HP 8452 diode array spectrophotometer. Elemental analysis was performed by Atlantic Microlab Inc. in Norcross, GA.

The irradiation measurements were done using a HeCd 325 nm laser or a 200 W high-pressure mercury lamp in combination with a filter setup. The desired wavelength was achieved by filtering the irradiation wavelength between 300 and 400 nm.

7.2. General procedure for fluorinated leucobases (2D–5D)

The corresponding aldehyde (1 eq), *N*,*N*-dimethylaniline (6 eq) and benzene (0.5 M with respect to the aldehyde) were placed in a flask fitted with a Dean–Stark trap and reflux condenser. *p*-Toluenesulfonic acid (0.1 eq) was then added to the mixture, and the solution refluxed. The reaction monitored by TLC until completion (typically 4–12 h depending on the aldehyde). Sometimes additional *p*-toluenesulfonic acid (up to 1 eq) had to be added in order to push the reaction to completion.

The reaction mixture was diluted with benzene to twice its volume and washed twice with 10% sodium bicarbonate solution. The benzene and most of the excess aniline were removed via azeotrope distillation with water. The resulting oil was then dissolved in warm hexanes and placed in a refrigerator to give crystals of the triarylmethane, which are normally good enough to be used without further purification. When needed, flash column chromatography on silica gel (typically 10:1 hexanes:ethyl acetate) was performed to further purify the products.

7.2.1. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-2-fluorophenylmethane (2D). Beige crystals. Mp=125–127°C. ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 12H), 5.69 (s, 1H), 6.69 (d, *J*=10.0 Hz, 4H), 6.96–7.18 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 40.7, 47.3, 112.5, 115.1 (d, *J*=21.9 Hz), 123.7 (d, *J*=3.7 Hz), 127.5 (d, *J*=7.3 Hz), 129.8, 130.8 (d, *J*=3.6 Hz), 131.4, 132.5 (d, *J*=14.6 Hz), 149.0, 160.7 (d, *J*=245.7 Hz). IR (NaCl): 2882, 1612, 1518, 1485 cm^{-1}. Elem. Anal. Calculated for $C_{23}H_{25}FN_2$: C, 79.27; H, 7.23; N, 8.04. Found C, 78.99; H, 7.39; N, 8.03. TLC (hexanes/ethyl acetate 5:1) R_f=0.47.

7.2.2. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-3-fluorophenylmethane (3D). Pale green crystals. Mp=99–100°C. ^{1}H NMR ($CDCl_3$): δ 2.92 (s, 12H), 5.37 (s, 1H), 6.68 (d, *J*=8.6 Hz, 4H), 6.81–6.91 (m, 3H), 6.98 (d, *J*=8.8 Hz, 4H), 7.16–7.26 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 40.7, 54.7, 112.5, 112.9, 116.2 (d, *J*=21.9 Hz), 125.0 (d, *J*=2.7 Hz), 129.4 (d, *J*=8.2 Hz), 129.8, 132.1, 148.2 (d, *J*=6.4 Hz), 149.0, 162.9 (d, *J*=242.9 Hz). IR (NaCl): 2880, 1612, 1517, 1349 cm^{-1}. Elem. Anal. Calculated for $C_{23}H_{25}FN_2$: C, 79.27; H, 7.23; N, 8.04. Found C, 79.22; H, 7.31; N, 7.99. TLC (hexanes/ethyl acetate 5:1) R_f=0.45.

7.2.3. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-4-fluorophenylmethane (4D). Pale green crystals. Mp=98–100°C. ^{1}H NMR ($CDCl_3$): δ 2.94 (s, 12H), 5.39 (s, 1H), 6.70 (d, *J*=8.4 Hz, 4H), 6.92–7.15 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 40.7, 54.2, 112.5, 114.7 (d, *J*=20.9 Hz), 129.8, 130.6 (d, *J*=8.2 Hz), 132.6, 141.1 (d, *J*=2.7 Hz), 148.9, 161.1 (d, *J*=242.1 Hz). IR (NaCl): 2880, 1613, 1518, 1348, 1220, 816 cm^{-1}. Elem. Anal. Calculated for $C_{23}H_{25}FN_2$: C, 79.27; H, 7.23; N, 8.04. Found C, 79.00; H, 7.36; N, 7.84. TLC (hexanes/ethyl acetate 10:1) R_f=0.28.

7.2.4. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-2,3,4,5,6-pentafluorophenylmethane (5D). Pale green crystals. Mp=118–120°C. ^{1}H NMR ($CDCl_3$): δ 2.94 (s, 12H), 5.72 (s, 1H), 6.78 (d, *J*=8.8 Hz, 4H), 7.07 (d, *J*=8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 40.6, 44.1, 112.4, 118.0–119.0 (m, 1C), 128.3, 129.2, 135.1–147.5 (m, 3C), 149.3. IR (NaCl): 1614, 1518, 1497, 1351, 1097 cm^{-1}. Elem. Anal. Calculated for $C_{23}H_{21}F_5N_2$: C, 65.70; H, 5.04; N, 6.66. Found C, 65.1; H, 5.13; N, 6.43. TLC (hexanes/ethyl acetate 10:1) R_f=0.42.

7.3. General procedure for fluorinated leuconitriles (2A–5A)

The corresponding triarylmethane (**2D**–**5D**) (1 eq) was dissolved in ethanol (0.1–0.2 M). Generally, the solution had to be heated for complete solvation to occur, and in some cases chloroform (no more than 10% of the total volume) was added to completely dissolve the material. Then 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (1.5 eq) was added in one portion, and the solution refluxed for 1 h. This dark solution was then removed from the heat source and allowed to cool while the potassium cyanide solution was being prepared. Potassium cyanide (20 eq) (**CAUTION**: KCN is a highly toxic material) was dissolved in a minimum amount of water, added to the reaction mixture, and the solution stirred for a period of 1 h.

The reaction mixture was dissolved in an equal volume of dichloromethane and extracted twice with 10% sodium bicarbonate solution and washed once with saturated sodium chloride. The organic phase was dried over magnesium sulfate and then concentrated. The resulting compound was then purified by column chromatography on neutral alumina (typically using 8:1 hexanes:ethyl acetate). The column chromatography was performed in a dark room to minimize conversion to the colored cation.

In some cases the 'purified' leuconitrile became colored upon evaporation of the eluant and had to be purified by a modification of the procedure used by Holmes.[7] The product (approximately 1–2 g) was dissolved in benzene, washed with dilute potassium cyanide (**CAUTION**: KCN is a highly toxic material), washed with sodium bicarbonate (10%), and then washed with dilute hydrochloric acid (less than 0.1 M). The HCl washings were repeated until all traces of the dye's color were gone. The organic phase (yellow in color) was then treated with decolorizing charcoal and filtered. The benzene was concentrated to 5 mL and then diluted with 20 mL of hexanes. This solution

generally produced colorless crystals although sometimes the procedure has to be repeated. The compounds are isolated as white or slightly colored crystals.

7.3.1. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-2-fluorophenyl acetonitrile (2A). White crystals. Mp=200–203°C. ^{1}H NMR ($CDCl_3$): δ 2.96 (s, 12H), 6.68 (d, *J*=8.8 Hz, 4H), 6.75–6.79 (m, 1H), 7.00–7.14 (m, 6H), 7.26–7.34 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 40.3, 51.8, 112.0, 116.4 (d, *J*=21.9 Hz), 122.6, 123.8 (d, *J*=3.7 Hz), 126.6, 129.0, 129.3, 130.0 (d, *J*=9.1 Hz), 130.3, 149.8, 160.5 (d, *J*=251.1 Hz). IR (NaCl): 2890, 2240, 1608, 1519 cm^{-1}. MS (EI) *m*/*z* 373, 278. Elem. Anal. Calculated for $C_{24}H_{24}FN_3$: C, 77.18; H, 6.48; N, 11.25. Found C, 77.05; H, 6.52; N, 11.15. TLC (hexanes/ethyl acetate 10:1 on alumina) R_f=0.26.

7.3.2. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-3-fluorophenyl acetonitrile (3A). Pale blue crystals. Mp=160–163°C. ^{1}H NMR ($CDCl_3$): δ 2.96 (s, 12H), 6.66 (d, *J*=8.8 Hz, 4H), 6.89–7.13 (m, 6H), 7.25–7.32 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 40.4, 55.6, 112.0, 114.6 (d, *J*=21.8 Hz), 116.0 (d, *J*=23.7 Hz), 123.7, 124.4 (d, *J*=2.8 Hz), 127.6, 129.4, 129.8 (d, *J*=8.1 Hz), 144.2, 149.8, 162.7 (d, *J*=245.7 Hz). IR (NaCl): 2890, 2234, 1610, 1519, 808 cm^{-1}. MS (EI) *m*/*z* 373, 278. Elem. Anal. Calculated for $C_{24}H_{24}FN_3$: C, 77.18; H, 6.48; N, 11.25. Found C, 77.19; H, 6.57; N, 11.17. TLC (hexanes/ethyl acetate 10:1 on alumina) R_f=0.33.

7.3.3. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-4-fluorophenyl acetonitrile (4A). White crystals. Mp=174–175°C. ^{1}H NMR ($CDCl_3$): δ 2.96 (s, 12H), 6.66 (d, *J*=9.2 Hz, 4H), 6.96–7.06 (m, 6H), 7.19–7.26 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 40.4, 55.3, 112.0, 115.2 (d, *J*=21.8 Hz), 124.1, 128.0, 129.4, 130.4 (d, *J*=7.3 Hz), 137.5, 149.8, 162.0 (d, *J*=246.6 Hz). IR (NaCl): 2805, 2230, 1609, 1516, 814 cm^{-1}. MS (EI) *m*/*z* 373, 278, 253. Elem. Anal. Calculated for $C_{24}H_{24}FN_3$: C, 77.18; H, 6.48; N, 11.25. Found C, 77.13; H, 6.54; N, 11.09. TLC (hexanes/ethyl acetate 2:1 on alumina) R_f=0.57.

7.3.4. Bis(4′,4″-*N*,*N*-dimethylaminophenyl)-2,3,4,5,6-pentafluorophenyl acetonitrile (5A). White crystals. Mp=175–176°C. ^{1}H NMR ($CDCl_3$): δ 2.97 (s, 12H), 6.67 (d, *J*=8.8 Hz, 4H), 7.30 (d, *J*=8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 42.3, 52.2, 114.1, 117.0–118.0 (m, 1C), 122.9, 126.8, 130.4, 137.0–150.0 (m, 3C), 152.2. IR (NaCl): 2924, 2236, 1611, 1521, 1488 cm^{-1}. MS (EI) *m*/*z* 445, 278, 138. Elem. Anal. Calculated for $C_{24}H_{20}F_5N_3$: C, 64.71; H, 4.53; N, 9.44. Found C, 65.69; H, 5.23; N, 8.63. TLC (hexanes/ethyl acetate 5:1 on alumina) R_f=0.50.

7.3.5. Tris(4′,4″,4‴-dimethylaminophenyl) acetonitrile (6A). This compound synthesized via a metathesis reaction using the commercial dye and potassium cyanide (**CAUTION**: KCN is a highly toxic material) in ethanol. Spectral characteristics matched those found in the literature.[8]

7.3.6. Tris(4′,4″,4‴-aminophenyl) acetonitrile (7A). Same as **6A**. ^{1}H NMR (CD_3CN): δ 4.23 (bs, 6H), 6.57–6.63 (m, 6H), 6.81–6.87 (m, 6H).

7.3.7. Trityl protected tris(4′,4″,4‴-aminophenyl) acetonitrile (8A). Compound **7A** (1.6 g, 5.1 mmol) was dissolved in 100 mL of anhydrous THF. Triethylamine (7.2 mL, 51 mmol) was added, and then a solution of trityl bromide (5.3 g, 16.1 mmol) in 20 mL of THF was added dropwise. The reaction mixture was stirred overnight. The THF was partially evaporated until about 40 mL was left, and the precipitate of triethylammonium bromide was filtered. Hexanes were added to the mother liquor, and the solid that precipitated was purified by cold recrystallization from methylene chloride–methanol. A second recrystallization from methylene chloride–hexanes provides 4.2 g of pure material. ^{1}H NMR ($CDCl_3$): δ 4.95 (s, 3H), 6.17 (d, *J*=8.4 Hz, 6H), 6.43 (d, *J*=8.4 Hz, 6H), 7.13–7.33 (m, 45 H). ^{13}C NMR ($CDCl_3$): δ 54.7, 71.6, 115.8, 124.4, 126.7, 127.8, 128.4, 129.0, 129.8, 145.2, 145.6. IR (NaCl): 3405, 3083, 1608, 1509, 699.

7.4. Victoria Blue Leuconitrile (9A)

This compound was synthesized via a metathesis reaction using the commercial dye and potassium cyanide (**CAUTION**: KCN is a highly toxic material) in ethanol. Spectral characteristics matched those found in the literature.[8]

7.4.1. Bis(4′,4″-dimethylaminophenyl)-(2-methylindol-3-yl)methane (10D). This compound was made via a slight modification of the following literature procedure.[12] A solution of dilute HCl (1 mL of concentrated acid in 25 mL of water) was added dropwise to a solution of 4,4′-bis-(dimethylamino)benzhydrol (2.01 g, 15.34 mmol) and 2-methylindole (4.15 g, 15.34 mmol) in 125 mL of methanol. This solution was refluxed for 90 min and then quenched with 1N NaOH. The precipitate that formed was filtered to provide 5.71 g (97% yield) of a slightly purple solid. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H), 2.90 (s, 12H), 5.58 (s, 1H), 6.67 (d, *J*=8.6 Hz, 4H), 6.88 (t, *J* =7.2 Hz, 1H), 7.00–7.26 (m, 7H), 7.73 (bs, 1H).

7.4.2. Bis(4-dimethylaminophenyl)-(2-methylindol-3-yl) acetonitrile (10A). The triarylmethane **10D** (1.01 g, 2.6 mmol) was placed in 20 mL of ethanol. After warming did not dissolve the solid, chloroform was added dropwise until a homogeneous solution was obtained. The 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.590 g, 2.6 mmol) was added slowly, and a vigorous reaction ensued. A slight excess of the DDQ was added to ensure complete conversion of starting material. The KCN (1.69 g, 26.0 mmol) (**CAUTION**: KCN is a highly toxic material) was added as a solution in water (5 mL). Dichloromethane was added, and this solution washed with aqueous $NaHCO_3$ (2× 50 mL), 0.1 M HCl (2×50 mL) and brine. The solution was concentrated and filtered through a small plug of alumina (3:1 hexanes: ethyl acetate) to provide the product. Recrystallization from ethanol provided 0.250 g (25%) of product. ^{1}H NMR ($CDCl_3$): δ 1.97 (s, 3H), 2.96 (s, 12H), 6.57–6.69 (m, 5H), 7.02–7.28 (m, 6H), 7.92 (bs, 1H). MS (EI) *m*/*z* 408.

7.4.3. Bis(4′,4″-dimethylaminophenyl)-(1-butyl-2-methylindol-3-yl)methane (11D). Under an inert atmosphere, the triarylmethane **10D** (0.345 g, 0.900 mmol) was dissolved in 10 mL of dry tetrahydrofuran. The solution was cooled to

0°C, and a 2.5 M solution of *n*-BuLi (0.40 mL, 0.99 mmol) was carefully added. The solution was stirred for 30 min and then cooled to −78°C. Butyl iodide (0.11 mL, 0.182 g, 0.99 mmol) was added, and the solution allowed to warm to room temperature. The reaction was monitored by thin layer chromatography and never did go to completion. Eventually, the reaction was quenched with water and extracted with ether. The organic layer was washed with brine and concentrated. The product was then purified by column chromatography (10:1 hexanes: ethyl acetate) to provide 0.335 g (85% yield) of product. ^{1}H NMR ($CDCl_3$): δ 0.83–0.98 (m, 3H), 1.26–1.42 (m, 2H), 1.67–1.75 (m, 2H), 2.25 (s, 3H), 2.90 (s, 12H), 4.04 (t, J=7.2 Hz, 2H), 5.60 (s, 1H), 6.65 (d, J=8.0 Hz, 4H), 6.81–6.89 (m, 1H), 7.01–7.09 (m, 6H), 7.21–7.26 (m, 1H).

7.4.4. Bis(4′4″-dimethylaminophenyl)-(1-butyl-2-methyl-indol-3-yl) acetonitrile (11A). The *N*-butylated triarylmethane **11D** (0.335 g, 0.762 mmol) was placed in 10 mL of ethanol and warmed to dissolve. The 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.207 g, 0.914 mmol, 1.2 eq) was added, and the solution refluxed for 1 h. A concentrated solution of KCN (1.48 g, 22.8 mmol, 30 eq) (**CAUTION**: KCN is a highly toxic material) in water (10 mL) was then added. Dichloromethane was added, and the layers separated. The organic layer was washed successively with saturated KCN (**CAUTION**: KCN is a highly toxic material), 1N NaOH, 0.01N HCl and then brine. The solution was concentrated and purified by chromatography (8:1 hexanes: ethyl acetate) on alumina that had been neutralized with 3% triethylamine in hexanes. All of the purification steps were performed in the absence of light. The product was isolated in 57% yield (0.201 g). ^{1}H NMR ($CDCl_3$): δ 0.85–0.99 (m, 3H), 1.26–1.44 (m, 2H), 1.68–1.76 (m, 2H), 2.11 (s, 3H), 2.98 (s, 12H), 4.07 (t, J=7.6 Hz, 2H), 6.21 (d, J=8.2 Hz, 4H), 6.75–6.82 (m, 1H), 7.03–7.29 (m, 7H). MS (EI) *m*/*z* 464, 449, 344.

7.5. Preparation of PMMA films

A solution (1.5 mL) containing 5 wt% polymethylmethacrylate (Aldrich, molecular weight ≈120 000 g mole^{-1}) and the color forming compound in butanone were cast on a glass slide (area of 482 mm^2). The concentration of the leuconitrile was adjusted to obtain an absorbance between 0.4 and 1 at 313 nm. The films were dried in a butanone atmosphere for 24 h.

7.6. Epoxy resin film preparation

Several drops of Cyracure UVR-6110 (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, Union Carbide) containing 0.75% of UVI-6974 (mixed triarylsulfonium hexafluoroantiminate salts, Union Carbide) and leuconitrile were laid down on a glass slide with a drawdown bar to obtain ≈100 micron liquid films. These films were scanned with a HeCd 44 mW laser to obtain polymer films of different color intensity. The overall dose was calculated based on the beam intensity and beam diameter.

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