

# Inverse photochromism of substituted triphenylmethane dyes in poly(vinyl alcohol) films

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## Abstract

The photochemistry of substituted triphenylmethane dyes was investigated in polymer films. Malachite green and brilliant green showed thermally stable photobleaching on visible light irradiation in poly(vinyl alcohol) films at room temperature. UV light irradiation of photobleached films recovered the blue colour. Such inverse photochromism is due to the binding of the dye cation and its counter anion to form a leuco structure, assisted by visible light, and the dissociation of the leuco structure by UV light irradiation. UV light irradiation also caused homolytic cleavage, leading to the formation of radicals, which resulted in a gradual decrease in the extent of colour change with increasing numbers of photoreaction cycles. Although symmetrically substituted dyes, such as crystal violet and ethyl violet, showed photobleaching on visible irradiation, no recolouration occurred on UV light irradiation.

**Keywords:** Inverse photochromism; Substituted triphenylmethane dyes; Poly(vinyl alcohol) films

## 1. Introduction

Light has many properties, such as wavelength, polarization and coherence (ultrashort pulse, focusing). In order to increase further the memory density in optical recording systems, so-called photon-mode optical memories, employing photochemical reactions instead of thermal reactions, and currently used in "optical" discs, are being developed. Photochromic systems, employing polymers or Langmuir–Blodgett (LB) films, have recently attracted considerable interest in view of their promising applicability to such purposes. The photochromism reported so far involves changes in chemical bonds, such as ring opening and closing in spiropyrans [1] and cis–trans isomerization in azobenzene [2]. These reactions may limit the thermal or cyclic stability and response time of optical recording, especially in the solid state.

We have studied the photochemical and photophysical properties of ion pair charge transfer complexes [3–17]. Using tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion as a counter ion of 4,4'-bipyridinium ions, we have achieved novel photochromism due to photoinduced electron transfer and thermal reverse reactions in organic solutions and polymer or LB films [3–17].

Triphenylmethane leuco derivatives exhibit photochromic behaviour [18,19]. On UV light irradiation in solution, many

colourless leuco compounds undergo heterolytic cleavage to form coloured dye cations. However, the colour gradually fades thermally as the leuco compound is re-formed. Recently, we have reported that the ion pair of triphenylmethane dye, malachite green, shows inverse photochromism, i.e. bleaching by visible light irradiation and thermal recovery in the dark, in organic solutions [20]. Such inverse photochromism has also been reported for crystal violet, having a similar structure to malachite green, in tetrahydrofuran, but the reaction mechanism has not yet been clarified [21]. In this paper, ion pairs of asymmetrically substituted triphenylmethane dyes are shown to undergo thermally stable inverse photochromism, i.e. bleaching by visible light irradiation and recovery by UV light irradiation, in polymer films. The effect of substituent groups was also studied.

## 2. Experimental details

### 2.1. Materials

The triphenylmethane dyes, malachite green oxalate ( $\text{MG}^+\text{OX}^-$ , Kishida Chemical Co., reagent grade, 1), brilliant green ( $\text{BG}^+\text{HSO}_4^-$ , Tokyo Kasei Co., specially prepared analytical reagent (SPAR), 2), crystal violet

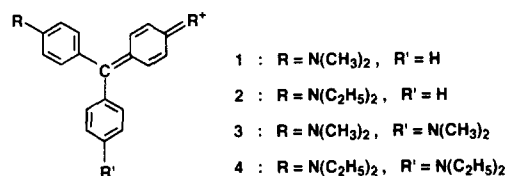


Fig. 1. Molecular structures of substituted triphenylmethane dyes.

(CV<sup>+</sup>Cl<sup>-</sup>, Tokyo Kasei Co., SPAR, **3**) and ethyl violet (EV<sup>+</sup>Cl<sup>-</sup> · 1/2ZnCl<sub>2</sub>, Tokyo Kasei Co., SPAR, **4**), were used without further purification. The molecular structures of the dyes are shown in Fig. 1. Dyes **1** and **2**, having two dialkylamino groups, are called asymmetrical dyes, while dyes **3** and **4** are called symmetrical dyes. Poly(vinyl alcohol) (PVA, Tokyo Kasei Co.) was used as a polymer matrix. Dye-dispersed aqueous solutions of PVA were prepared by sonication for about 1 min with slight heating. The weight ratio of dye to PVA is 1:2000. Transparent coloured polymer films were obtained by casting these polymer solutions onto a quartz plate.

## 2.2. Measurements

Samples were irradiated in air using a 150 W Hg–Xe lamp (Hamamatsu Hg–Xe lamp, L2570) through an L-39 cut-off filter ( $\lambda_{\text{ex}} > 365$  nm, Toshiba Glass) and an IR cut-off filter (Melles Griot 03FC6167) for visible light irradiation, or a bandpass filter ( $\lambda_{\text{ex}} = 260$  nm, Melles Griot 03FIU002) for UV light irradiation. The photoreaction was monitored by a JASCO Ubest-55 UV–visible spectrophotometer at room temperature. The fluorescence spectra were recorded with a SHIMADZU RF-5000 fluorescence spectrophotometer. Electron spin resonance (ESR) spectra were measured with a JEOL JES-RE1X high-resolution spectrometer. The data were analysed by a personal computer (NEC PC-9801 UF). The reduction potentials of the dyes were measured by cyclic voltammetry (Nikko Keisoku NPGS-301). The voltammograms were measured in acetonitrile using a saturated calomel electrode (SCE) as reference.

## 3. Results and discussion

### 3.1. Asymmetrical dyes

Triphenylmethane dyes exhibit inverse photochromism in PVA films, the details of which depend on the number of substituents as shown below. The absorption spectra of **1** in PVA aqueous solution and PVA film are shown in Fig. 2. In PVA aqueous solution (Fig. 2(a)), the absorption bands of **1** are observed at 312, 425 and 620 nm, which are similar to those in aqueous solution without PVA. These bands exhibit red shifts and a decrease in absorbance in PVA film after the evaporation of water as shown in Fig. 2(b). A new absorption peak appears in the UV region at 260 nm in PVA film. The absorbance of this new peak increases, while the other absorp-

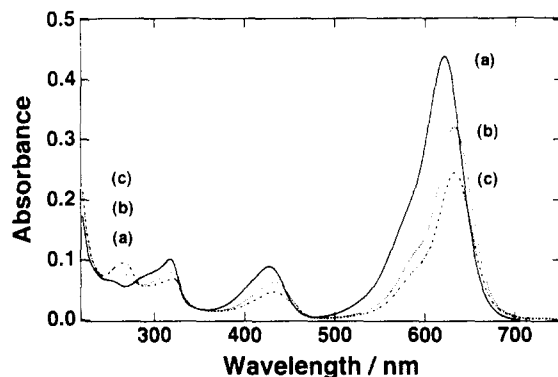


Fig. 2. Absorption spectra of **1** in aqueous solution containing PVA (a), in as-cast PVA film (b) and dried PVA film (c).

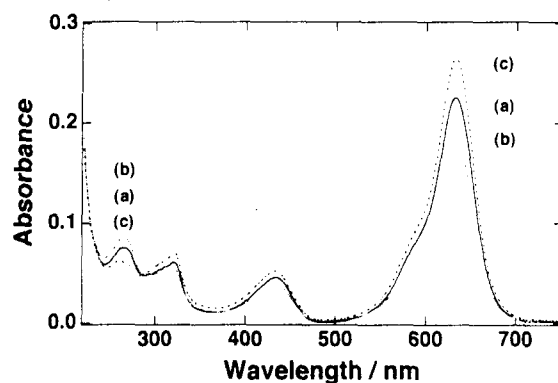


Fig. 3. Absorption spectra of **1** in PVA film before irradiation (a), after visible light irradiation ( $\lambda_{\text{ex}} > 365$  nm) for 30 min (b) and after UV irradiation ( $\lambda_{\text{ex}} = 260$  nm) for 5 min (c) at room temperature.

tion bands of **1** decrease, on further drying of the PVA film (Fig. 2(c)); an isosbestic point is observed at 280 nm. The new absorption peak is similar to that of leuco esters, observed for **1** in low polarity solvents, such as 1,2-dimethoxyethane (DME) [20]. These results show that the MG<sup>+</sup> and OX<sup>-</sup> contact ion pairs form a leuco structure in PVA film in a similar manner to that observed in DME solution, i.e. by bond formation between the central carbon of MG<sup>+</sup> and the carboxyl group of OX<sup>-</sup>. The microenvironment around **1** in PVA film should be much less polar than in aqueous solution. The equilibrium between bond formation and contact ion pairs has been reported by several workers for carbocation and carboanion ion pairs in solution [22–26].

Visible light irradiation ( $\lambda_{\text{ex}} > 365$  nm) of PVA film containing **1** causes photobleaching. The absorption spectra are shown in Fig. 3 for PVA films before and after irradiation for 30 min. The characteristic absorption of **1** decreases and the UV absorption at 260 nm increases on visible light irradiation. The photobleaching strongly suggests that the equilibrium between the contact ion pairs and the leuco structure varies due to the increased reduction potential of MG<sup>+</sup> by photoexcitation as mentioned below. The photobleached state is stable and no thermal recovery is observed in PVA film, whereas the visible band recovers in DME solution after about 10 h at 20 °C in the dark [20]. The time-dependent absorbance

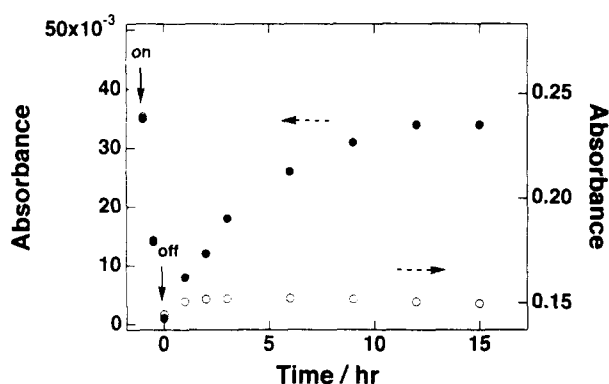


Fig. 4. Absorbance changes of **1** during photoexcitation (between on and off) and subsequent storage in the dark, monitored at 631 nm at room temperature: in DME solution (10  $\mu$ M, ●); in PVA film (dye:PVA = 1:2000, ○).

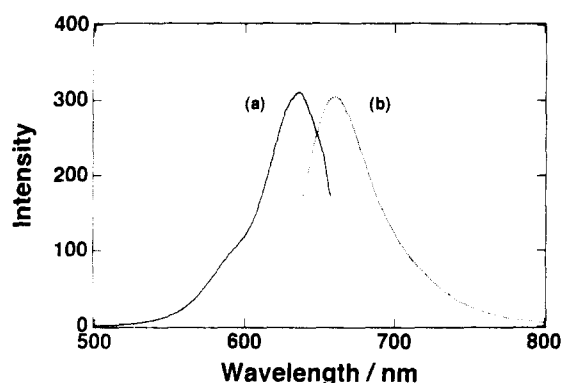


Fig. 5. Fluorescence excitation ( $\lambda_{em} = 659$  nm) (a) and fluorescence ( $\lambda_{ex} = 631$  nm) (b) spectra of **1** in PVA film.

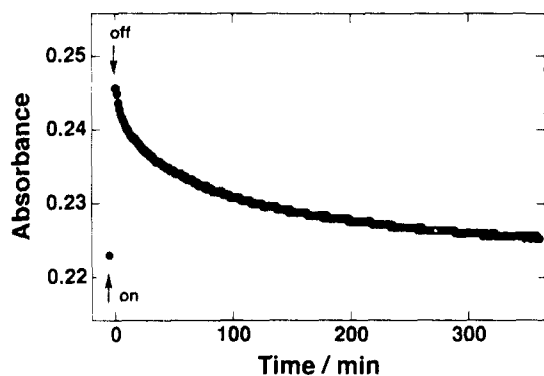


Fig. 6. Time dependence of the absorbance of **1** at 631 nm in the dark in PVA film after UV irradiation for 5 min at room temperature.

changes at 631 nm during photoexcitation and subsequent storage of **1** in the dark at room temperature in DME solution and PVA film are shown in Fig. 4. The stability of the bleached state is probably due to the frozen molecular motion of  $MG^+$  and the less polar microenvironment in the PVA film. The fact that the steady fluorescence of  $MG^+$  with a peak at 659 nm is observed in PVA film, as shown in Fig. 5, supports the former. In aqueous solutions of **1**, no steady fluorescence is observed due to a very rapid rotational motion of the phenyl rings ( $\tau_s < 2$  ps) [27,28]. The reduction poten-

tial of **1**, [ $MG^+/MG^{\cdot-}$ ], has been determined to be  $-0.60$  V vs. SCE in acetonitrile. The corresponding value at the excited singlet state, [ $(MG^+)^*/MG^{\cdot-}$ ], is estimated to be  $+1.28$  V vs. SCE from the fluorescence peak wavelength.

The absorption spectrum of PVA film on UV light irradiation ( $\lambda_{ex} = 260$  nm) for 5 min is shown in Fig. 3(c). The UV absorption at 260 nm almost disappears and the visible absorption of **1** increases. This result shows that the ionic dissociation of the leuco structure occurs on UV light irradiation. Coloured dye cations photogenerated in PVA film on UV irradiation are not as stable as the leuco structure formed by visible irradiation. The visible absorption bands, before UV irradiation, are recovered after storage for several hours at room temperature as shown in Fig. 6. The microenvironment in the PVA film is not polar as indicated by the formation of the leuco structure from contact ion pairs. Therefore the concentration of polar (ionic) structures generated by UV irradiation will decrease to the equilibrium value at room temperature in PVA film as shown schematically in Fig. 7.

UV and visible light irradiations were carried out repeatedly in PVA films containing **1** or **2**. The absorbance changes

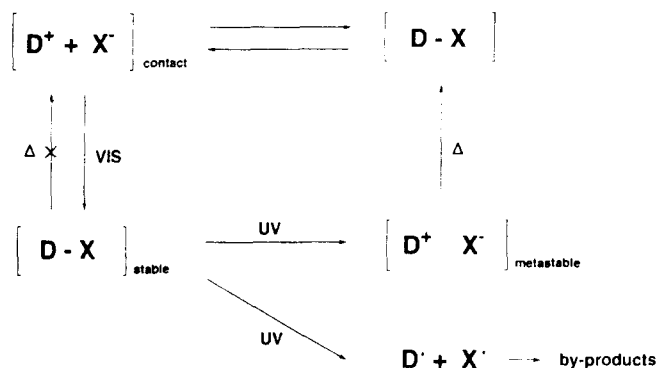


Fig. 7. Schematic representation of the reaction scheme on UV and visible irradiation in PVA film:  $D^+$  and  $D^{\cdot-}$  denote triphenylmethane dye and its reduced form,  $X^-$  and  $X^{\cdot-}$  denote the counter anion and its oxidized form,  $D-X$  is the leuco structure,  $\Delta$  represents heat and a cross on the arrow indicates that the reaction does not occur.

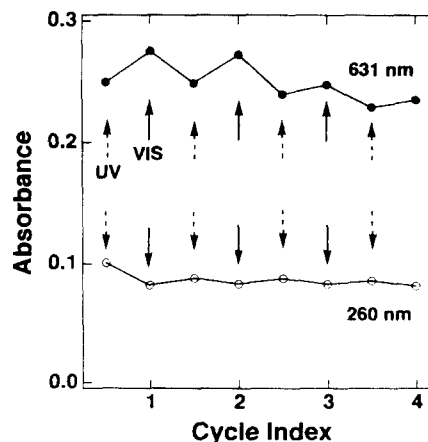


Fig. 8. Absorbance changes at 631 nm (●) and 260 nm (○) of **1** in PVA film during repeated UV and visible irradiation.

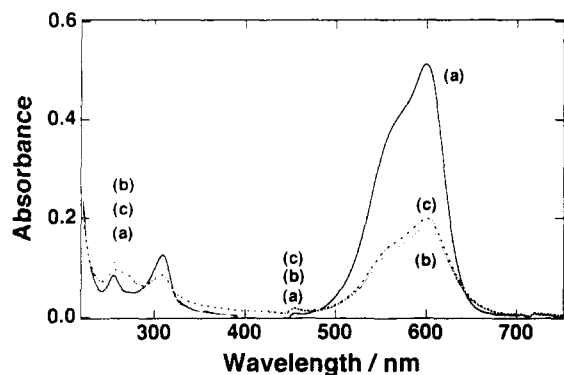


Fig. 9. Absorption spectra of **3** in PVA film before irradiation (a), after visible light irradiation ( $\lambda_{\text{ex}} > 365$  nm) for 30 min (b) and after UV irradiation ( $\lambda_{\text{ex}} = 260$  nm) for 5 min (c) at room temperature.

of **1** at 631 nm and of the leuco structure at 260 nm are shown in Fig. 8 as a function of the cycle index. On UV light irradiation, the absorption band at 631 nm increases with a decrease in the absorption band at 260 nm. On subsequent visible irradiation, the absorption band at 631 nm decreases and the absorption band at 260 nm increases. Similar photobleaching and recolouration are observed in dye **2**. The counter ions ( $\text{OX}^-$ ) of **1** are exchanged with chloride anions. Such inverse photochromism was repeated in PVA films. However, the extent of the colour changes decreases gradually during repeated irradiation. Visible irradiation causes only photobleaching. However, ESR measurements reveal that UV light irradiation causes not only heterolytic cleavage to form coloured cationic dyes, but also homolytic cleavage to form neutral radicals. A schematic representation of the reaction mechanism in the present system is summarized in Fig. 7. The equilibrium between the contact ion pairs and the leuco structure in PVA film is shown at the top of Fig. 7. Although the probability of homolytic cleavage seems to be considerably lower than that of heterolytic cleavage, the effect is increased with an increasing number of photoreaction cycles.

### 3.2. Symmetrical dyes

The third dialkylamino group in symmetrical dyes **3** and **4** causes considerable changes in the absorption and fluorescence spectra. While asymmetrical dyes exhibit two absorption bands in the visible region, symmetrical dyes exhibit only one. Asymmetrical dyes do not show steady fluorescence, unlike symmetrical dyes. For symmetrical dyes, rotational motion is probably prevented due to the steric hindrance of the three phenyl rings substituted with dialkylamino groups, which causes steady fluorescence.

The absorption spectrum of **3** in PVA film is shown in Fig. 9. The spectrum in PVA film before irradiation is the same as that in aqueous solution. The leuco structure is not formed in PVA film in contrast with the asymmetrical dyes shown in Fig. 2. Leuco bond formation is much less favoured in symmetrical dyes due to the steric hindrance and decreased elec-

trophilic nature of the central carbon of symmetrical dyes containing three electron-donating substituents, i.e. dialkylamino groups. The reduction potential of **3** has been determined in acetonitrile to be  $-0.77$  V vs. SCE, which is more negative by 0.17 eV than that of **1**. These results indicate that the electrophilic nature of **3** is lower than that of **1**.

The absorption spectra of PVA film containing **3** before visible irradiation for 30 min and after UV irradiation for 5 min are shown in Fig. 9. On visible irradiation, the characteristic absorption of **3** decreases and the UV absorption at 260 nm increases in a similar manner to that observed for **1**. However, a new absorption band at 390–480 nm also appears, which was assigned to crystal violet (CV) radical by Leaver [29]. On UV light irradiation, the absorption band at 260 nm decreases, but the visible absorption band increases only slightly as shown in Fig. 9(c). The 320–480 nm band also increases on UV light irradiation. These results show that heterolytic cleavage to form coloured **3** is less important than homolytic cleavage to form CV radicals.

Accurate molecular design and control of the microenvironment around triphenylmethane dye, to decrease the homolytic cleavage without affecting the visible light-induced photobleaching, are needed for the practical use of the present system as a photon-mode high-density optical memory based on inverse photochromism.

## 4. Conclusions

Asymmetrical triphenylmethane dyes in PVA film show photobleaching on visible light irradiation, which is thermally stable at room temperature. The recovery of the blue colour is observed on UV light irradiation of the photobleached films. Such inverse photochromism is caused by visible light-assisted binding of the dye cation and counter anion in contact ion pairs and by heterolytic dissociation of the leuco structure. UV light also produces radicals, to some extent, via homolytic cleavage, which gradually decreases the reversibility with increasing number of photoreaction cycles. Symmetrically substituted triphenylmethane dyes show photobleaching but no recolouration.

## References

- [1] E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara and K. Fukuda, *Thin Solid Films*, **133** (1985) 21.
- [2] S.S. Sandhu, Y.P. Yianni, C.G. Morgan, D.M. Taylor and B. Zaba, *Biochem. Biophys. Acta*, **86** (1986) 253.
- [3] T. Nagamura and K. Sakai, *J. Chem. Soc., Chem. Commun.*, (1986) 810.
- [4] T. Nagamura and K. Sakai, *Chem. Phys. Lett.*, **141** (1987) 553.
- [5] T. Nagamura and K. Sakai, *Ber. Bunsenges. Phys. Chem.*, **92** (1988) 707.
- [6] T. Nagamura and K. Sakai, *J. Chem. Soc., Faraday Trans. 1*, **84** (1988) 3529.
- [7] T. Nagamura and K. Sakai, *J. Chem. Soc., Chem. Commun.*, (1988) 1035.

- [8] T. Nagamura, K. Sakai and T. Ogawa, *Thin Solid Films*, 179 (1989) 375.
- [9] T. Nagamura and K. Sakai, *Ber. Bunsenges. Phys. Chem.*, 93 (1989) 1432.
- [10] T. Nagamura and Y. Isoda, *J. Chem. Soc., Chem. Commun.*, (1991) 72.
- [11] T. Nagamura and S. Muta, *J. Photopolym. Sci. Technol.*, 4 (1991) 55.
- [12] T. Nagamura, Y. Isoda, K. Sakai and T. Ogawa, *Thin Solid Films*, 210/211 (1992) 617.
- [13] K. Sakai, S. Muta and T. Nagamura, *J. Photopolym. Sci. Technol.*, 5 (1992) 557.
- [14] T. Nagamura, Y. Isoda and K. Sakai, *Polym. Int.*, 27 (1992) 125.
- [15] T. Nagamura, S. Muta and K. Sakai, *J. Photopolym. Sci. Technol.*, 5 (1992) 561.
- [16] T. Nagamura, *Mol. Cryst. Liq. Cryst.*, 224 (1993) 75.
- [17] T. Nagamura, H. Sakaguchi, S. Muta and T. Ito, *Appl. Phys. Lett.*, 63 (1993) 2762.
- [18] R. McNair, *Photochem. Photobiol.*, 6 (1967) 779.
- [19] R.C. Bertelson, in G.H. Brown (ed.), *Photochromism. Techniques of Chemistry*, Vol. III, Wiley-Interscience, New York, 1971, p. 294.
- [20] H. Kawai and T. Nagamura, *J. Photopolym. Sci. Technol.*, 7 (1994) 107.
- [21] E.D. Owen, S.A.R. Hosseini and R.J. Breakspere, *Chem. Ind.*, 20 (1979) 706.
- [22] E.B. Troughton, K.E. Molter and E.M. Arnett, *J. Am. Chem. Soc.*, 106 (1984) 6726.
- [23] E.M. Arnett, B. Chawla, K.E. Molter, K. Amarnath and M. Healy, *J. Am. Chem. Soc.*, 107 (1985) 5288.
- [24] E.M. Arnett and K.E. Molter, *J. Phys. Chem.*, 90 (1986) 383.
- [25] K. Komatsu, S. Aonuma, K. Takeuchi and K. Okamoto, *J. Org. Chem.*, 54 (1989) 2038.
- [26] E.M. Arnett, K.E. Molter, E.C. Marchot, W.H. Donovan and P. Smith, *J. Am. Chem. Soc.*, 109 (1987) 3788.
- [27] V. Sundstrom and T. Gillbro, *J. Chem. Phys.*, 81 (1984) 3463.
- [28] R.A. Engh, J.W. Petrich and G.R. Fleming, *J. Phys. Chem.*, 89 (1985) 618.
- [29] I.H. Leaver, *Photochem. Photobiol.*, 16 (1972) 189.