

## FEATURES OF THE PHOTOALIGNMENT OF DISODIUM BIS-[(4-HYDROXY-3-CARBOXYLATE-6-METHYL)PHENYLAZO]-5,5'-DIOXOBENZOTHIOPHENE IN THIN FILMS

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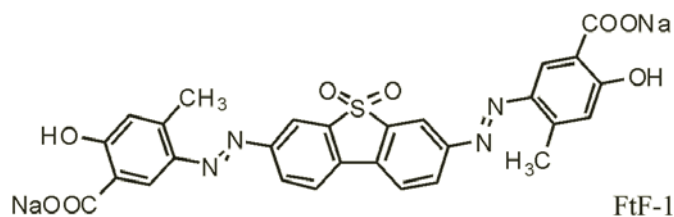
*Thin films and multilayer thin-film coatings based on the new dichroic azo dye disodium bis[(4-hydroxy-3-carboxylate-6-methyl)phenylazo]-5,5'-dioxobenzothiophene (FtF-1) were produced by the spin-coating method. The optical properties and morphology of the FtF-1 films depended on the formation conditions and used solvents. Reversible photo-induced dichroism was observed in films obtained by spin-coating of FtF-1 solutions in DMF and aqueous polyvinylpyrrolidone on quartz substrates upon irradiation with plane-polarized light ( $\lambda = 450$  nm,  $I = 15$  mW/cm<sup>2</sup>). The anisotropic properties of the FtF-1 films were caused by trans-cis-isomerization of the irradiated dye molecules.*

**Keywords:** disodium bis-[(4-hydroxy-3-carboxylate-6-methyl)phenylazo]-5,5'-dioxobenzothiophene, polyvinylpyrrolidone, thin film, spin-coating, photoirradiation, spectral properties, absorption dichroism, morphology.

**Introduction.** Organic azo dyes are promising for producing optically anisotropic films with given operating characteristics [1–3]. Thin-film materials based on them possess high azimuthal anchoring energy with liquid crystals [4] and are thermally stable [5]. Reversible *trans-cis*-isomerization of molecular configurations and their orientation and formation of an anisotropic structure occurred in azo-dye films through the action of polarized light [6, 7]. The development of new photo-oriented azo dyes and the study of the effect of the formation conditions on the optical properties and morphology of thin-film materials are critical for producing high-quality optical polarization elements and devices. A method for forming optically anisotropic multilayer thin-film coatings by spin-coating was developed and the effect of the polymeric matrix on the optical properties and morphology of the coatings was studied previously using the industrial azo dye Brilliant Yellow [8].

The goal of the present work was to study features of the photo-orientation and morphology of thin films of the new synthetic azo dye disodium bis-[(4-hydroxy-3-carboxylate-6-methyl)phenylazo]-5,5'-dioxobenzothiophene as a function of their formation conditions.

**Experimental.** The dye FtF-1 was prepared by the literature method [9] via diazotization of benzidinesulfone and subsequent coupling of the diazo product with 4-methylsalicylic acid:



The structure of FtF-1 that was purified as before [10] was confirmed by IR, UV, PMR, and <sup>13</sup>C NMR spectroscopy. IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3441 (OH), 2923, 1456, 1380 (C–H), 1638 (C=O), 1583 (C=C), 1301, 1162 (SO<sub>2</sub>). UV spectrum (H<sub>2</sub>O,  $\lambda_{\max}$ ): 424 nm. PMR spectrum (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 2.65 (s, 6H), 6.65 (s, 2H), 8.24 (m, 6H), 8.41

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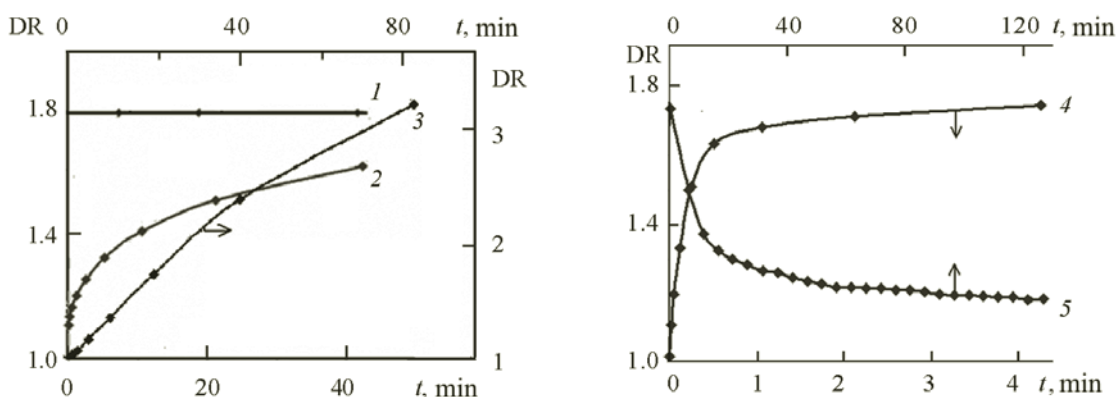


Fig. 1. Kinetics of dichroic ratio change for films of FtF-1 (H<sub>2</sub>O) (1, 2), FtF-1 (DMF) (3), and FtF-1 (PVP) (4, 5) dried at 95 (1, 3–5) and 130°C (2) upon irradiation by plane-polarized light (1–4) and in the dark (5).

(d,  $J = 8$  Hz, 2H). <sup>13</sup>C NMR spectrum (125 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 17.63, 112.94, 117.37, 117.37, 117.67, 118.58, 124.11, 129.98, 130.43, 138.89, 140.59, 144.86, 154.17, 170.53, 170.76.

Polyvinylpyrrolidone (PVP) [Plasdone K-12, molecular weight (MW) =  $4 \cdot 10^3$ ] and polymethylmethacrylate (PMMA) (LSOM grade) were used without further purification. Polystyrene (PS, characteristic viscosity  $[\eta] = 0.35$ , MW =  $8.1 \cdot 10^4$ ) was reprecipitated by EtOH from a solution (5%) in benzene. Solvents were purified by the usual methods [11]. Thin-film coatings of FtF-1 were produced and studied as before [8]. Solutions of FtF-1 (~0.1 mL) in H<sub>2</sub>O, aqueous PVP, and DMF were placed on the substrate and spun at 800 and 1300 rpm for 3 and 60 s. FtF-1 films were dried for 5 min at 50°C and then for 30 min at 95°C. Solutions (5% and 10%) of PMMA or PS in toluene were placed (~0.1 mL) on a dye layer, spun at 800 and 2000 rpm for 3 and 60 s, and dried under the same conditions as the FtF-1 films in order to produce isotropic layers in multilayer films. Deposition of dye and polymer layers were alternated sequentially during formation of the multilayer composition. FtF-1 films were irradiated by plane-polarized light (blue LED with  $\lambda = 450$  nm and  $I = 15$  mW/cm<sup>2</sup>) and full-spectrum light from a DRT-1000 lamp. IR spectra of films were recorded on a Bruker TENSOR 27 IR-Fourier spectrometer. Elemental compositions of the films were determined by electron-probe microanalysis using a Genesis 2000 accessory for a Philips SEM-515 scanning electron microscope.

**Results and Discussion.** Absorption spectra of films precipitated from FtF-1 solutions in H<sub>2</sub>O ( $\lambda_{\max} = 416$  nm) and DMF ( $\lambda_{\max} = 450$  nm) displayed a hypsochromic shift of the absorption maxima relative to those of the solutions in H<sub>2</sub>O ( $\lambda_{\max} = 424$  nm) and DMF ( $\lambda_{\max} = 503$  nm). Apparently, dye molecules in the thin films formed H-aggregates. The short-wavelength shift of the absorption band was indicative of this. The ability of organic dyes to aggregate during spin-coating of their solutions was noted earlier [12, 13].

The polarization properties of films produced from aqueous solutions of FtF-1 [FtF-1(H<sub>2</sub>O)] depended considerably on the presence of traces of solvent in them. Thus, film dried at 95°C was anisotropic in the initial state. The dichroic ratio (DR), which is a measure of the film optical anisotropy ( $DR = A_{\perp}/A_{\parallel}$ , where  $A_{\perp}$  and  $A_{\parallel}$  are the absorption of plane-polarized probe radiation in the directions perpendicular and parallel to the polarization of the exposing radiation), was 1.8 and did not change upon irradiation by plane-polarized light (Fig. 1, curve 1). However, film dried at 130°C exhibited slight dichroism in the initial state and was polarized during irradiation (curve 2).

Apparently, impurities of H<sub>2</sub>O had a plasticizing action, facilitated intra- and intermolecular movement in the hard FtF-1 film, and assisted directional orientation of dye molecules during film formation and the generation of anisotropy in it. The direction of the film anisotropy was dictated by radial centrifugal forces arising during rotation of the substrate at a constant angular velocity. The film became harder after removing traces of solvent at 130°C. Molecular motions in it were hindered and decreased the probability of orienting FtF-1 molecules and the appearance of anisotropy.

Films of FtF-1(H<sub>2</sub>O) dried at 95°C remained anisotropic for a long time (the DR value did not change over one month of storage in air). A bilayer coating [FtF-1(H<sub>2</sub>O)]/PS that was dried at 95°C was also optically anisotropic in the initial state and did not change during prolonged storage.

Absorption of an FtF-1 film dried at 130°C changed slightly during irradiation with the full spectrum of a DRT-1000 high-pressure Hg lamp for 200 min ( $A_{200\text{min}}/A_0 = 0.86$ ) (Fig. 2, curve 4) and remained practically unchanged during storage

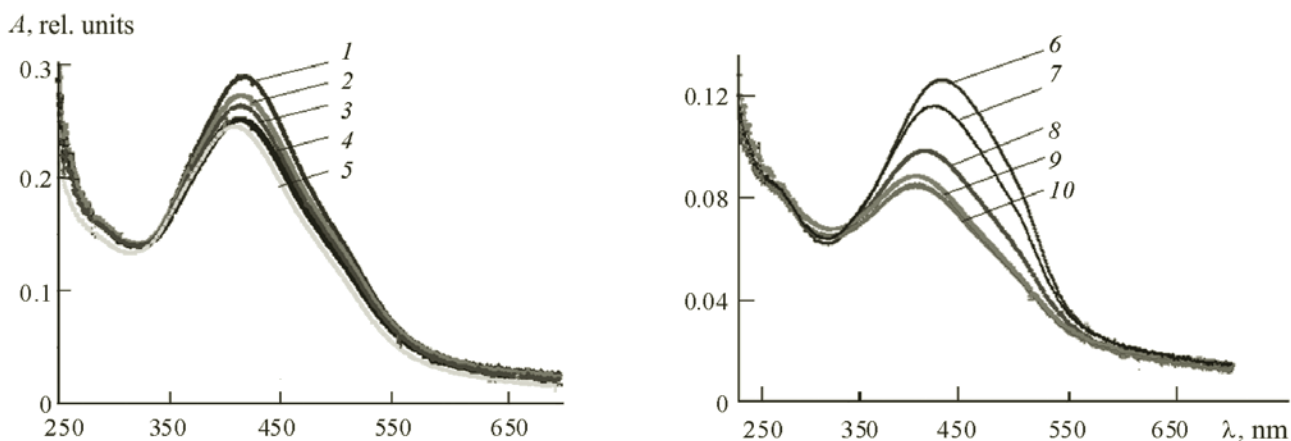


Fig. 2. Optical density change of unirradiated (1, 6) films of FtF-1(H<sub>2</sub>O) (1–5) and FtF-1(DMF) (6–10) and those irradiated by the full spectrum of an Hg lamp for 80 (2), 140 (3), 200 (4), 20 (7), 60 (8), and 120 min (9); spectra of films irradiated for 200 and 120 min followed by storage in air for 17 and 4 d (5 and 10).

of the irradiated film for 17 d (curve 5). UV and IR spectra of the initial ( $\lambda_{\max} = 416$  nm) and irradiated ( $\lambda_{\max} = 414$  nm) FtF-1 films were identical. Therefore, the dye chemical structure in the thin film formed from the aqueous solution was stable to the action of the light.

However, films formed from FtF-1 solutions in DMF [FtF-1(DMF)] and dried at 95°C were optically isotropic and were polarized during irradiation (Fig. 1, curve 3).

The DR values for films deposited from dye solutions in DMF were greater than those of films deposited from its aqueous solutions with identical formation and irradiation conditions. For example, DR = 3.33 for FtF-1(DMF) and 1.58 for FtF-1(H<sub>2</sub>O) with 0.45 mass% FtF-1 in the starting solutions and irradiation with polarized light for  $t = 42$  min. The DR values decreased with increasing dye concentration in the initial DMF solution and were 5.05, 3.22, and 3.21 for [FtF-1] = 0.45, 0.71, and 1.17 mass%, respectively ( $t = 82$  min). FtF-1(DMF) films were less stable than those deposited from aqueous solutions. This was confirmed by the hypsochromic shift of  $\lambda_{\max}$  and the greater decrease of their optical density during exposure to the full spectrum of the DRT-1000 lamp (Fig. 2, curves 6–9). Thus,  $A_{120\text{min}}/A_0 = 0.67$  for FtF-1(DMF) film and 0.91 for FtF-1(H<sub>2</sub>O) film.

The generation of photo-induced dichroism during exposure to plane-polarized light (Fig. 1, curve 3), the hypsochromic shift of  $\lambda_{\max}$ , and the presence of an isosbestic point in the spectrum of FtF film irradiated by the full-spectrum of the Hg lamp (Fig. 2, curves 6–9) were consistent with *trans-cis*-isomerization of the dye molecules [14] in the FtF-1(DMF) film. The reverse *cis-trans*-isomerization was very slow. Thus, the DR value (3.22) did not change after storage of the polarized film in air for 3 d. It is noteworthy that FtF-1(DMF) films became cloudy and crystallized on the substrate during prolonged storage.

It was found [15] that the generation and disappearance of photo-induced anisotropy could be intentionally controlled if organic azo dyes embedded in polymeric matrices were used as the anisotropic media. Then, the matrix played a decisive role in fabricating the photoanisotropic material. Achievement of the maximum anisotropy and reverse dark relaxation of the dye from the *cis*- into the *trans*-form depended significantly on the chemical activity (reactivity) of the used polymer. A solution of PVP in H<sub>2</sub>O was selected as the chemically active matrix for FtF-1. PVP was capable of complexing dye molecules owing to the pyrrole N atom. Isomerization was facilitated by the interaction with polarized light quanta [16]. The FtF-1 film was formed by spin-coating of an aqueous PVP solution (5%) containing dye (0.5 mass%).

The spectrum of a film of FtF-1 embedded in a PVP matrix [FtF-1(PVP)] showed a bathochromic shift of the absorption maximum ( $\lambda_{\max} = 454$  nm) relative to that of a film of pure dye ( $\lambda_{\max} = 416$  nm). The shift of the absorption maximum by 38 nm may have been due to the formation of an FtF-1:PVP complex because the PVP film was transparent in the studied spectral range. FtF-1(PVP) film dried at 95°C was optically isotropic. Photo-induced dichroism arose during irradiation by polarized light (Fig. 1, curve 4). A peculiarity of the photo-induced dichroism of FtF-1 in the PVP matrix was that the induced anisotropy grew very rapidly. The DR reached 1.6 in ~30 s and then increased insignificantly with increasing exposure. The reverse dark relaxation was relatively slow (curve 5). The film returned to the initial state (DR = 1) after 7 d.

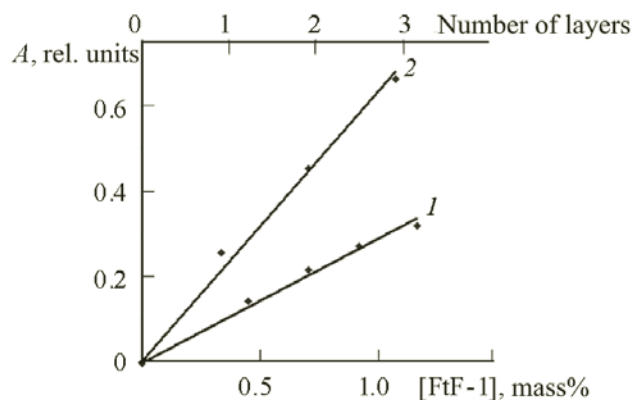


Fig. 3. Absorption of FtF-1(DMF) films as a function of dye concentration in starting solution (1) and number of FtF-1 layers in a five-layer coating FtF-1(DMF)/PMMA (2).

The calculated linear dichroism values [ $d = (A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$ ] at the absorption maximum for films formed under identical production ([FtF-1] = 0.5 mass%) and irradiation ( $t = 42$  min) conditions were 0.22 [FtF-1(H<sub>2</sub>O)], 0.20 [FtF-1(PVP)], and 0.54 [FtF-1(DMF)]. The results indicated that the film optical properties depended considerably on the nature of the solvent.

A solution of PMMA (5%) in toluene was used to form isotropic layers in a multilayer composite coating based on FtF-1(PVP). The PVP improved the compatibility of the anisotropic and isotropic layers during production of the multilayer coatings. The optical density of a five-layer coating of FtF-1(PVP)/PMMA depended linearly on the number of dye layers.

Isotropic layers in the multilayer coating based on FtF-1(DMF) were produced from PMMA (10%) in toluene because the polymer layer obtained from a 5% solution did not protect the underlying dye layer from dissolving. The lack of a linear dependence between the absorption and the number of FtF-1 layers was evidence of this. The optical density of FtF-1(DMF) and multilayer FtF-1(DMF)/PMMA coatings was linearly dependent on the FtF-1 concentration in the initial solution and the number of dye layers in the coating (Fig. 3). This enabled multilayer coatings with given thicknesses and optical properties to be formed. The DR values for monolayer (DR = 2.3) and five-layer (DR = 1.9) coatings of FtF-1(DMF)/PMMA under identical exposure conditions differed little. It could be assumed that FtF-1 molecules in isolated layers of the multilayer coating had the same orientations because the dichroism ratio depended on the angular distribution of dye molecules in the layer plane.

The morphology of FtF-1 films depended on their formation conditions, in particular, the nature of the solvent and matrix in which the dye was embedded. Thus, FtF-1 film spin-coated on a Si substrate from a solution (0.5%) in H<sub>2</sub>O and dried at 95°C had an oriented "fibrous" structure (fibrillar) (Fig. 4a). The film surface was covered by needle-like formations ~2.8 μm long (Fig. 4b) and ~24 nm high (Fig. 4c). Aggregates (Fig. 4d) were observed if the drying temperature was increased to 130°C and residual water was removed from the surface. These may have been due to impurities of Na<sub>2</sub>CO<sub>3</sub> and NaOH that were used to synthesize the dye and remained in it after production. This hypothesis was confirmed using electron-probe microanalysis (Fig. 4e and 4f), which showed a higher sodium concentration in the aggregates (81.95 mass%, 71.89 at%) than in the film (16.30 mass%, 9.78 at%). The FtF-1 film morphology was practically unchanged after irradiation by the full spectrum of the DRT-1000 lamp. The irradiated film was slightly rougher ( $R_{ms} = 5.6$  nm) than the initial film ( $R_{ms} = 4.9$  nm).

Supramolecular fibrils and spherulite-like particles (Fig. 4g) formed on the surface of FtF-1(DMF) films produced under the same conditions as for the FtF-1(H<sub>2</sub>O) film ([FtF-1] = 0.45 mass%, 95°C) [17]. Composite films formed from aqueous PVP solutions were transparent, highly uniform (Fig. 4h), and almost smooth ( $R_{ms} = 0.4$  nm). The morphology of the FtF-1(PVP) film changed considerably after irradiation by plane-polarized light. The dye molecules in the PVP matrix were probably oriented in a certain manner by the light and formed long branched aggregates that were randomly situated on the film surface (Fig. 4i). The roughness of film irradiated for 1 h increased to 1.4 nm. However, its surface evened out during storage and returned to the initial value. Thus,  $R_{ms} = 0.4$  nm after storage for a week and changed little with time. Similar morphology changes were also observed in unirradiated FtF-1(PVP) film that was exposed to light for a long time. Photo-induced molecular movement of dye AD-1 (4,4'-bis[4-N,N-di(n-butyl)aminophenylazo]biphenyl) and modification of its nanostructure by optical radiation were demonstrated [18].

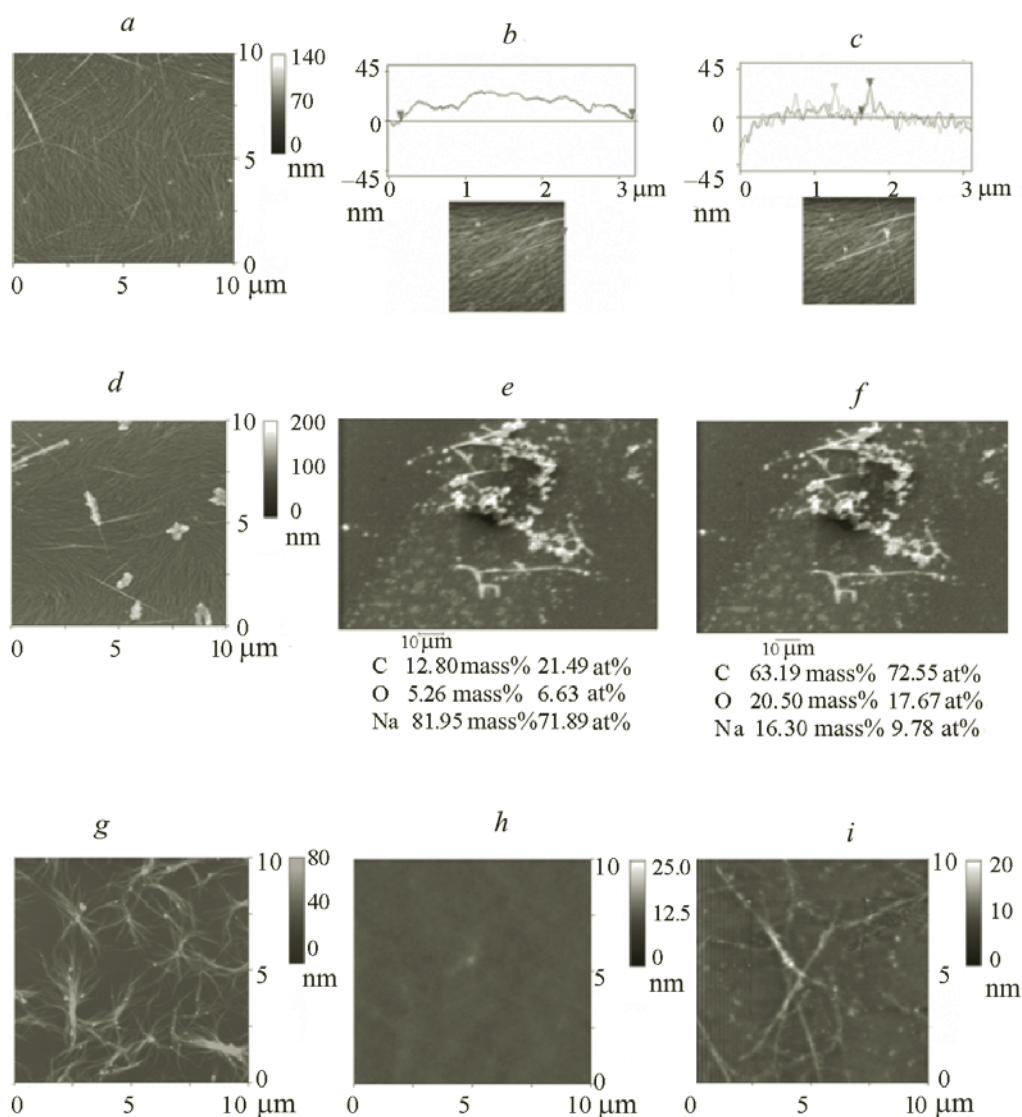


Fig. 4. AFM (a–d, g–i) and SEM (e, f) images of the surface topology of FtF-1(H<sub>2</sub>O) (a–f), FtF-1(DMF) (g), and FtF-1(PVP) (h, i) films; drying temperature 95 (a–c, g–i) and 130°C (d–f); starting film (h) and that after irradiation for 1 h by plane-polarized light (i).

**Conclusions.** The optical properties and morphology of FtF-1 films spin-coated from dye solutions depended on the formation conditions and used solvents. Film prepared from FtF-1 in an aqueous solution was anisotropic in the initial state. However, film formed from FtF-1 in DMF solution and composite film with FtF-1 embedded in a PVP matrix were optically isotropic and exhibited reversible photo-induced dichroism upon irradiation with plane-polarized light ( $\lambda = 450 \text{ nm}$ ,  $I = 15 \text{ mW/cm}^2$ ).

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