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# Reversible multi-coloring reaction of spironaphtooxazine controlled by long-chain molecule

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## ABSTRACT

A novel reversible multi-colored (red, violet, blue and yellow) film was realized using a typical photochromic dye (the color former) and docosylphosphonic acid (the color developer). A mixture of the color former/color developer exhibiting reversible multi-coloring reactions was controlled by heat-treatment of the solid phase. The structure and crystalline state of the film mixtures were investigated by UV–vis spectroscopy, X-ray diffraction and high-resolution electron diffraction measurements. The color of the films was controlled by the structural type of the photomerocyanine-form (protonated zwitterionic, zwitterionic and quinoid). The mechanism of the multi-coloring reaction was concluded to be the chemical combination of color formers and color developers, which produces red and violet colors, and when the coloration-temperature acts to separate the color formers from the color developers, yellow color appears. Furthermore, the color of the film changed from yellow to blue upon 360 nm light irradiation.

## 1. Introduction

Recycling of used papers is a very important problem. In recent years, a large amount of paper has been used for the temporary display of digitized information. With respect to waste reduction, various reversible image formation systems have been proposed and developed [1–15]. Spirooxazines are currently used in many commercial applications, such as ophthalmic lenses, sunglasses [16], optical memory and photo-optical switching devices [17], due to their reversible colored–decolored reaction under ultraviolet light, visible light or acid [18–20]. Spirooxazine consists of two heterocyclic moieties linked together by an $sp^3$ spirocarbon atom. Irradiation of ultraviolet light and/or temperature increase causes cleavage of the relatively weak spirocarbon–oxygen bond followed by conformational rearrangement, leading finally to ring-opened colored isomers, the so-called photomerocyanine-form (PMC-form). The PMC-form reverts to the closed-ring isomer (spiropyran form; SP-form) through a thermally induced ring closure reaction; fading of the colored isomers occurs on a timescale of seconds to minutes at room temperature. It is well known that the geometry of such a conjugated PMC-form of spirooxazine can vary between two extreme resonance structures [21]; the non-polar quinoid structure dominates in low polarity solvents and the zwitterionic structure is more stable in polar media [22] as shown in Scheme 1. Therefore, spiropyrans have the chromophoric ability to exhibit multi-color change due to a change in the ambient polarity. In a previous publication, our group reported reversible coloration (colorless/black) reaction using leuco dye and *N*-(4-hydroxyphenyl)docosanamide, crystal structure and its mechanism [23].

In this study, mixed films containing spirooxazine dye and long-chain alkyl phosphate were investigated in order to establish a multi-coloring reaction in the solid phase for rewritable paper. Docosylphosphonic acid, which is a long-chain alkyl phosphate, was used as an acidic compound (referred to as the color developer). Spironaphtooxazine, which has the quinoid or zwitterionic type structures, can be controlled by stimuli such as external heating and interaction with the color developer in the solid phase, and as a most typical spirooxazine, was used as the color former.

## 2. Experimental

1,3,3-Trimethylspiro[indoline-2,3′-naphtho[2,1-b][1,4]oxazine] (SNO) and docosylphosphonic acid (P22, mp 110 °C) were used as the color former and color developer, respectively, the two components of multi-colored films. The films were prepared by the following procedure. A mixture of SNO/P22 (1/3; molar ratio) was sandwiched between two cover glass slides (thickness 0.12–0.17 mm) and was melted on a hot plate maintained at 102 °C. The films were then rapidly cooled by immersion in an ice-bath. Irradiation with a Xe lamp (MAX-301,

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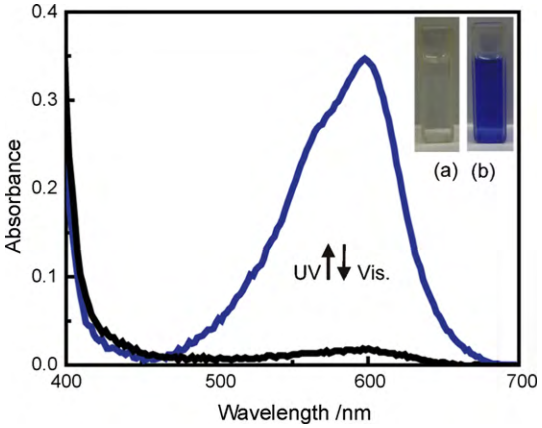


**Fig. 1.** Absorption spectra of a toluene solution of SNO in the SP-form (conc. $3.5 \times 10^{-5}$ M, black line) and photostationary PMC-form (blue line) under irradiation with 360 nm light. The inset shows photographs of the toluene solution (a) before and (b) after irradiation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Asahi Spectra) at specific excitation wavelengths ($\lambda = 360$ nm and >420 nm) was used to generate a photoisomer. UV–visible (UV–vis) absorption spectra of the solution and films were recorded using a spectrometer (Shimadzu UV-2200). The crystal structures of the films were investigated using X-ray diffraction (XRD; Rigaku Rint2000, Cu-Kα radiation) and electron diffraction on a transmission electron microscope (TEM; Hitachi H-7100). The films for TEM observations were prepared on mica substrates coated with carbon films prepared by vacuum deposition. The specimen film was separated with the carbon film from the mica substrate and transferred to a microgrid. Selected-area and high-resolution electron diffraction patterns were obtained from a specific area several μm and about 100 μm in diameter, respectively.

## 3. Results and discussion

Fig. 1 shows the change in the UV–vis absorption spectrum of SNO in toluene solution ($3.5 \times 10^{-5}$ M) before and after irradiation with 360 nm light. Upon irradiation, the solution changed from colorless (SP-form) to blue (PMC-form) and a broad absorption band appeared with a maximum at 598 nm. It is well known that eight geometric arrangement of PMC-form were recognized around the methine bridge. The geometric arrangement of the most stable isomer was determined as *trans–trans–cis* (TTC) form in this timescale [24,28]. The absorption band was assigned to $\pi$–$\pi^*$ transitions of the quinoid structure PMC-form. After irradiation was ceased, the absorption intensity of the PMC-form decreased immediately within approximately 10 s at room temperature. Upon irradiation with visible light of >420 nm, the absorption band also decreased immediately within approximately 2–3 s. In addition, the behaviors of PMC-form in various polar solvents were confirmed by the solvatochromism. The solvatochromism depends on the difference in the dipole moment between the singlet ground state and the singlet excited state of the chromophore. Reichardt introduced the transition energy (expressed in kcal/mol) in order to explain the effect of $\lambda_{\max}$ on the solvatochromism of pyridium-*N*-phenoxide betaine dye in various solvents. This parameter is referred to as the $E_T$ value, which is related with the $\lambda_{\max}$ of absorption spectra according to the following equation [25]:

$$E_T(\text{kcal mol}^{-1}) = \frac{2.859 \times 10^4}{\lambda_{\max}(\text{nm})}$$

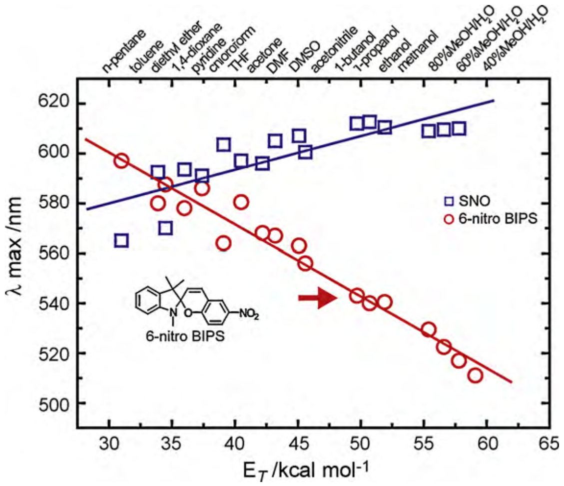


**Fig. 2.** $\lambda_{\max}$ of the PMC-form versus $E_T$ for SNO and 6-nitro BIPS. The obtained linear plot shows an approximate relationship between these plots.

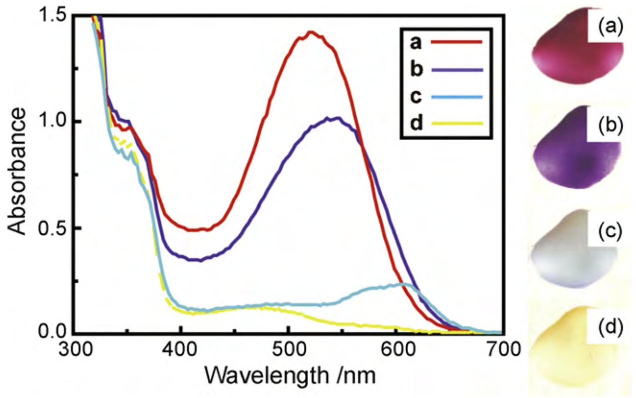


**Fig. 3.** UV–vis absorption spectra and photographs of the SNO/P22 mixture films; (a) rapid cooling after heating at 110 °C, (b) reheating at 60 °C, (c) upon UV light irradiation, and (d) overheating at 80 °C.

Fig. 2 shows a linear plot of $\lambda_{\max}$ for the PMC-form versus the $E_T$ parameters of various solvents. $\lambda_{\max}$ of the PMC-form of SNO has a positive gradient, but that of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)indole] (6-nitro BIPS) has a negative gradient. These results indicate that the PMC-form of SNO, which is stable as the quinoid type in solution, exhibits a long-wavelength shift (bathochromic shift); therefore, the singlet excited state of the PMC-form is more polar than the singlet ground state [26]. The energy gap between the ground state and the exited state can be widened, due to different stabilization with ambient polarity; thus, the electronic states of these molecular structures have different dipole moments [27]. As a result, the PMC-form in polar solvent exhibited the bathochromic shift. On the contrary, the PMC-form of 6-nitro BIPS is stabilized as the zwitterionic structure, so that its solvatochromism exhibits a short-wavelength shift (hypsochromic shift). Therefore, SNO has the ability of solvatochromism, in that its PMC-form has either molecular structure (quinoid or zwitterionic types) [28]. Therefore, it is possible that in non-polar solvents, the PMC-form of SNO exists as the quinoid structure, but SNO can undergo thermal ring opening to the corresponding zwitterionic structure upon dissolution in a polar solvent. It is suggested that SNO can exhibit negative solvatochromism similar to 6-nitro BIPS when in acidic media. When the SNO/P22 molten films were heated on a hot plate at 110 °C, the films completely melted and the molten mixture turned red. The red color gradually disappeared during slow cooling in air; however, the color remained when the molten mixture was cooled rapidly by immersion into an ice-bath (Fig. 3(a)). The red films have an absorption

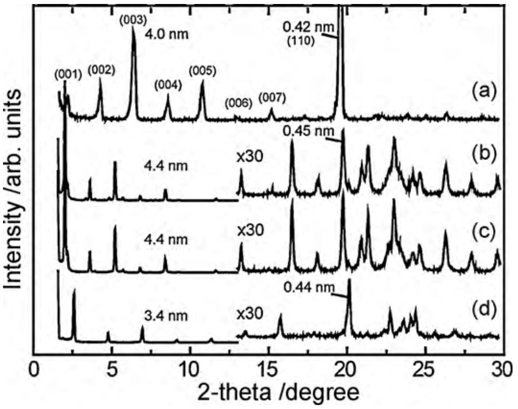


**Fig. 4.** XRD patterns of: (a) P22 powder and P22 films (b) rapidly cooled after heating at 110 °C, (c) reheated at 60 °C, and (d) overheated at 90 °C.

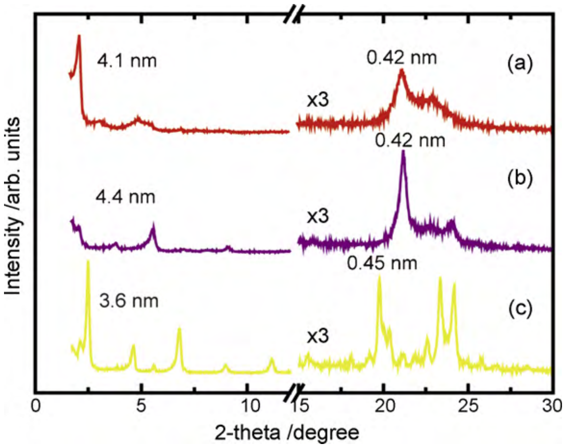


**Fig. 5.** XRD patterns of SNO/P22 mixture films (a) heated at 110 °C and rapidly cooled (colored red), (b) reheated at 60 °C (colored violet), and (c) overheated at 80 °C (colored yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

band with a maximum at 520 nm and a hypsochromic shift, which is due to the effect of acid on the PMC-form. A similar absorption spectrum for the PMC-form in acidic media has been reported [22]. This structure can be attributed to a protonated PMC-form (H—PMC-form), which is due to the interaction between the short conjugated zwitterionic structure and a proton of the P22 developer. When the red films were reheated at 60 °C for 60 s and cooled spontaneously in air, violet colored films were obtained that showed absorption spectra centered at 537 nm, which can be attributed to the non-protonated zwitterionic PMC-form similar to the absorption peak of 6-nitro BIPS dissolved in a polar solvent, as shown in Fig. 3(b). On the other hand, when the violet films were overheated at 80 °C for 10 s and cooled spontaneously in air, the color of the films was changed from violet to yellow. The yellow colored films were assigned to the SP-form, which has an absorption band with a maximum at 470 nm, as shown in Fig. 3(d). Multi-coloring thermochromic reactions were possible by repeating the above performance at least 10 times. Furthermore, upon irradiation with 360 nm light, the color of the films changed from yellow to blue and a broad absorption band with a maximum at 598 nm appeared (Fig. 3(c)). The spectral changes indicated photochromism, and this absorption band was assigned to the quinoid structure PMC-form, which was similar to that in solution. This molecular structure can be attributed to the PMC-form, which had no interaction with the P22 color developer. After stopping the UV light irradiation, the absorption intensity of the PMC-form gradually decreased within approximately 1 h at room temperature. These results indicate that the structures of the PMC-form, either zwitterionic or quinoid type, were determined by the interaction with the P22 color developer.

Fig. 4 shows XRD patterns of P22 powder and films. The XRD pattern of P22 powder (Fig. 4(a)) shows several diffraction peaks in the low angle region ($2\theta = 2.2°$, 4.3°, 6.4°, 8.6°, 10.8°, 13.0° and 15.2°). These diffraction peaks correspond to the lattice spacing, which is estimated to be approximately 4.0 nm, and its higher order reflections. The molecular length of P22 calculated using WinMopac V2.0 is 2.9 nm, which suggests that P22 molecules are stacked in the crystal with a head-to-head layered structure, similar to a fatty acid, as indicated by the reflections from the (0 0 l) planes of the P22 crystal [23]. P22 powder shows an intense peak in the high angle region ($2\theta = 21.0°$), which corresponds to short spacing (0.42 nm), and is the reflection from the (1 1 0) plane of the orthorhombic P22 crystal system. This intense peak indicates the existence of lamellar structure and loose packing of the long-chain alkyl groups. Fig. 4(b)–(d) shows XRD patterns of the P22 films that were treated by (b) rapid cooling after heating at 110 °C, (c) reheating at 60 °C and (d) overheating at 90 °C, with peaks corresponding to long spacing of 4.4, 4.4 and 3.4 nm and their higher order reflections, respectively. These results indicate that P22 forms at least three crystal phases. The intense peaks in the high angle region ($2\theta = 19.7°$, 19.7° and 20.1°, respectively) correspond to lamellar structures with short spacings of approximately 0.45, 0.45 and 0.44 nm, respectively. Fig. 5 shows XRD patterns of the (a) red, (b) violet and (c) yellow films. In the red film (Fig. 5(a)), an intense peak in the low angle region ($2\theta = 2.1°$) and a broad peak in the high angle region ($2\theta = 21.0°$) correspond to long (4.1 nm) and short (0.42 nm) spacings. The broad peak corresponding to the loose packing of long-chain alkyl groups, which is similar to a typical liquid crystal structure. On the other hand, the violet film shown in Fig. 5(b) is different from the red film. A peak in the low angle region ($2\theta = 5.5°$), which is reflection from the (0 0 3) plane and a broad peak in the high angle region ($2\theta = 21.2°$) correspond to long and short spacings of 4.4 and 0.42 nm, respectively. Fig. 5(c) shows the XRD pattern of the yellow film with an intense peaks in the low angle region ($2\theta = 2.5°$, 4.6°, 5.5°, 6.8°, 9.0° and 11.1°), which are reflected from the (0 0 l) plane and its higher order reflections corresponding to a long spacing of 3.6 nm, and a broad peak in the high angle region ($2\theta = 19.7°$) indicates short spacing (0.45 nm). These diffraction peaks in the high angle region are quite similar to that of overheated P22 films, which were highly crystalline and with rigid stacking similar to the P22 powder.

In order to clarify the fine structural change in SNO/P22 multi-coloring reaction, electron diffraction measurements were carried out. Fig. 6 shows electron diffraction patterns of SNO/P22 multi-colored films. There are several Debye–Scherrer rings in the high-resolution electron diffraction patterns of the red and violet films (Fig. 6(a) and (b)), which indicate that the red and violet films have microcrystalline structure. The ring patterns of the red and violet films correspond to 0.23, 0.25, 0.38 and 0.42 nm spacings of the microcrystal and are in good agreement with the XRD patterns in the high angle scattering region. Consequently, it was concluded that the crystallized P22 molecules in SNO/P22 films have a lamellar structure similar to the pristine P22 film. On the other hand, the selected area electron diffraction pattern of the yellow film shows Laue spots obtained from overheated P22 films with SNO, as shown in Fig. 6(c). These spots are reflected from several planes of the P22 orthorhombic crystal system. The P22 molecules in the yellow films seem to crystallize with the same crystal structure as the pristine P22 films (Fig. 6(d)). When the color formers and color developers are chemically combined in the microcrystal, red and violet colors appear. However, the coloration-temperature acts to separate the color formers from the color developers, so that when P22 molecules crystallize, the yellow color appears. Fig. 7

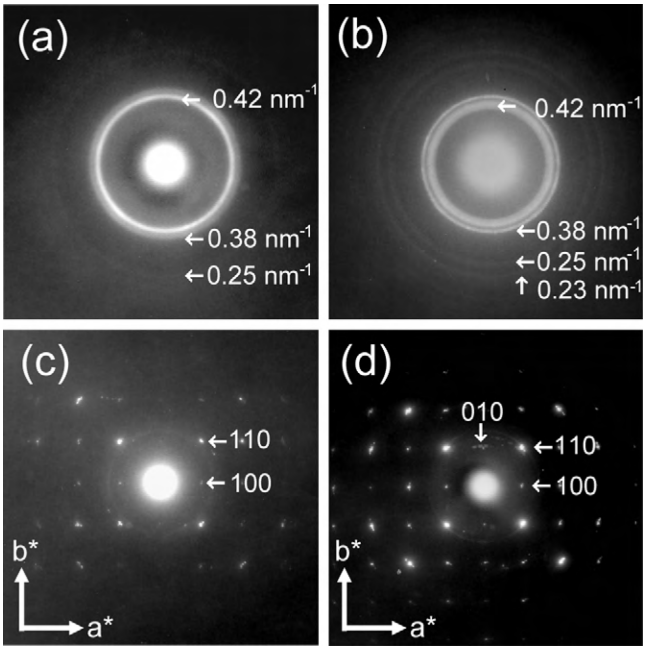
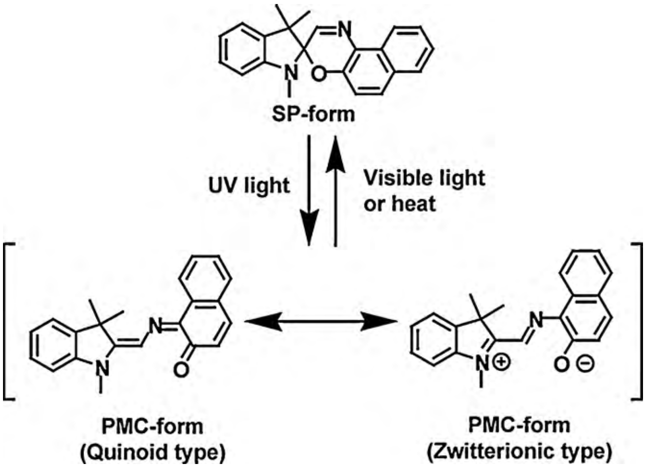


**Fig. 6.** ED patterns of SNO/P22 mixture films (a) heated at 110 °C and rapidly cooled (colored red), (b) reheated at 60 °C (colored violet), (c) overheated at 80 °C (colored yellow), and (d) a P22 film overheated at 90 °C. (a) and (b): high-resolution electron diffraction, (c) and (d): selected-area electron diffraction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Scheme 1.** The reversible photochromic reaction of SNO.

shows a proposed mechanism for the SNO/P22 multi-coloring reaction summarized from these results. SNO/P22 films were melted by heating at 110 °C. The absorption spectrum of the red film with $\lambda_{max}$ centered at 520 nm has a molecular structure of the PMC-form with a protonated zwitterionic structure of the PMC-form and a proton of phosphate acid groups of P22. The absorption spectrum of the film remains the same as that of the molten state upon rapid cooling after melting. The molecular structure of the PMC-form is also the same as that of the molten state. The crystal structure in the red film is a disordered microcrystal. When the red film is continuously reheated at 60 °C, P22 molecules slightly activate and release to SNO. The absorption spectrum of the violet film with $\lambda_{max}$ centered at 537 nm indicates a molecular structure of the PMC-form with a non-interaction zwitterionic structure. The crystal structure of the violet film is almost the same as the red film. Furthermore, for the violet film overheated at 80 °C, the absorption spectrum of the film returns to the initial yellow color with $\lambda_{max}$ centered at 470 nm and the molecular structure is revealed to be the SP-form by thermal cycloreversion. The P22 molecules activate further and are individually crystallized. Upon irradiation of the yellow film with UV light, the absorption spectrum is changed to blue with $\lambda_{max}$ centered at 598 nm and with a molecular structure of the quinoid PMC-form without change of the crystalline state. The quinoid PMC-form obtained disappears within approximately 1 h at room temperature and the PMC-form returns to the SP-form. Finally, the yellow film melts by overheating at 110 °C and changes to the reddish molten state. Reversible thermal and photoresponse were confirmed several times with depression of the absorption intensity to less than 30%.

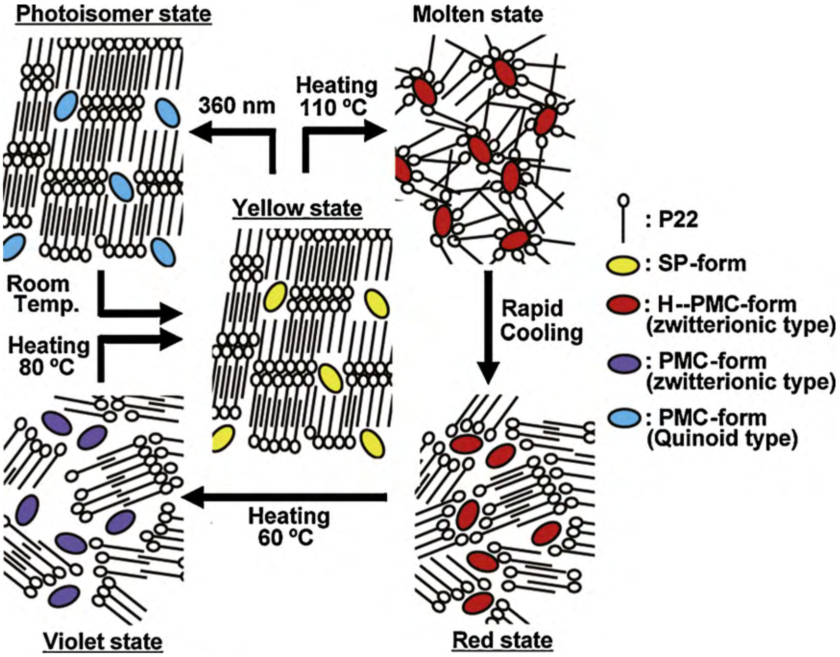


**Fig. 7.** Schematic representation of the mechanism for the multi-coloring reaction of SNO/P22 mixture films.

## 4. Conclusions

A novel reversible multi-colored film was realized using SNO and P22. A mixture of SNO/P22 showing a reversible multi-coloring/decoloring reaction was controlled by heat-treatment of the solid phase. XRD and HRED observations revealed that the P22 molecules are stacked in a head-to-head layered structure. The color of the films was controlled by the structural type of the PMC-form (protonated zwitterionic, zwitterionic and quinoid). If a key black state was obtained instead of the violet state in this system, it would be expected that in the future all basic colors (CMYK) could be established by a single molecule.

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