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Reverse photochromism of spiropyran in silica

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ABSTRACT

The high thermal stability of the photomerocyanine-form (PMC-form) of spiropyran (SP) dispersed in perhydropolysilazane (PHPS), which converted to silica at ambient temperature, was investigated. PHPS was converted to silica by the de-ammonium reaction with water vapor within approximately 48 h. The structure of the converted silica was not only SiO_2, but also partially uncondensed Si–OH and O–H. The PMC-form with high thermal stability was attributed to the protonated form, which was produced by intermolecular hydrogen bonding between oxide anion generated by cleavage of C–O bonds and the partially uncondensed Si–OH and O–H of silica. The protonated PMC-form was directly generated from the SP-form without UV light irradiation, because the singlet ground state of the PMC-form (PMC_0) is lower than that of the SP-form (SP_0) in silica. In this mechanism, the singlet ground state of the protonated PMC-form ($H\cdots PMC_0$), which is significantly stabilized by silica, had polarity similar to water. The stabilization of the PMC-form was attributed to hydrogen bonding between silica and direct generation from the SP-form by reverse photochromism.

1. Introduction

Light-induced reversible transformation between two isomers with different absorption spectra is referred to as photochromism [1–4]. Two isomers differ from one another not only in their absorption properties, but also in refractive indices, dielectric constants, oxidation–reduction potentials, and geometric structures. Therefore, these properties can be reversibly switched upon irradiation with an appropriate wavelength of light. Spiropyrans (SPs) are well-known photochromic compounds that have attracted much interest with respect to both the fundamental elucidation of photochemical reactions and their potential application to optical memory and photo-optical switching devices [5–10]. The application of SPs to such devices is restricted by the short lifetime of the open photomerocyanine-form (PMC-form), which thermally reverts to the closed colorless spiropyran-form (SP-form) (Scheme 1). Many studies have been performed to investigate the lifetime and/or dynamics of the thermal reversion process by measuring the static absorption/fluorescence [11–14] and the time-resolved absorption/fluorescence [15–20] during the last couple of decades. Obviously these studies contributed to solve the complicated mechanism of PMC-form. For practical applications, the thermally unstable PMC-form must be dispersed in a solid matrix, because PMC-form in their crystalline state is usually inactive. In the last two decades, various methods have been reported for the dispersion and stabilization of the PMC-form. Stabilization of the PMC-form has mainly focused on metal complex [21], and SP has been dispersed in rigid matrices such as polymers [22], sol–gels [23], organogels [24], inorganic particles [25], clay interlayers [26] and mesoporous silica [27], whereby the mobility of the PMC-form is restricted. PMC-form can be either covalently linked to a polymer backbone or dispersed in a polymer matrix, and can also be entrapped within two- and three-dimensional networks or intercalate within inorganic nanoparticles. Polysilazane derived silica have been intensively studied in recent years [28]. Perhydropolysilazane (PHPS) is considered to be a highly efficient ceramic precursor. Coatings prepared on commercially available PHPS substrates are curable by reaction with water vapor at ambient temperature. PHPS can be converted to silica without lattice defects and with a density of 1.3 g/cm^3 [29]. Moreover, at temperatures of 80–120 °C the curing rate can be increased by the treatment of PHPS films with pyridine and NH_3 [30]. Using methyl-substituted piperidine, alkylamines or acids as catalysts, PHPS curing at room temperature is claimed to provide dense coatings that are impermeable to oxygen, which thereby prevent the oxidation of metal surfaces [31]. Quite recently, Yamano and Kozuka reported a mechanism for the interaction of the PMC-form with a silica matrix, in which the absorption process was enhanced by reverse photochromic reaction [32]. We previously reported that the high thermal stability of the PMC-form in silica has the possibility of being protonated by interaction between oxide anions generated by cleavage of the C–O bond, ethanol or the propanoic acid linked *N*-position, and oxygen of Si–O–Si in silica [33]. However, the detailed mechanisms of hydrogen bonding and thermal stabilization are yet to be clari-

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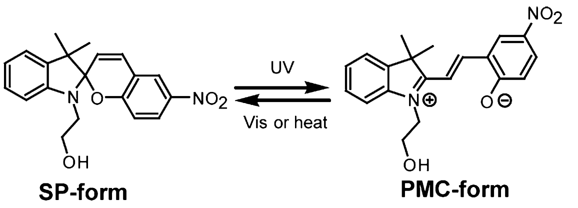

Scheme 1. Reversible photochromic reaction of the SP- and PMC-forms.

fied. In this report, we have proposed a mechanism regarding the generation of the protonated PMC-form from investigations using UV–vis, infrared (IR) and X-ray photoelectron (XPS) spectroscopies, in addition to an energy diagram for the mechanism.

2. Experimental

1′-(2-Hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[1(2H)-benzopyran-2,2′-indoline] (Sp) was synthesized by a coupling reaction with Fischer's base 1-(2′-hydroxyethyl)-2,3,3-trimethylindolenium iodide and 5-nitrosalicylaldehyde according to the previous report [33]. A commercially available *m*-xylene solution of PHPS (5%, NL110, Clariant Japan Co.) was used as a precursor to prepare the silica film. The PHPS *m*-xylene solution containing 10^{-4} M Sp was spun at 4000 rpm on a fused silica and Si(1 0 0) substrate, the latter of which was for FT-IR measurements. In the case of using poly(vinyl alcohol) (PVA; Nacalai Tesque Co.) as a matrix, a PVA dimethylsulfoxide solution with same concentration of SP was prepared by spin-coating. The as-spun film was stored in the dark at room temperature while all measurements also performed in this paper were carried out in the dark to inhibit thermal reversion. The excitation wavelength (λ = 360 nm) from a Xe lamp (MAX-301, Asahi Spectra) was used to generate the PMC-form. UV–vis absorption spectra were recorded with a Shimadzu UV-2200 spectrophotometer. IR spectra were recorded using a Jeol FT/IR-660Plus under vacuum conditions. XPS spectra were recorded with Shimadzu ESCA3400, using an Al Kα monochromator X-ray source operated at 10 kV and 20.0 mA under pressures of 10^{-5} Pa, and with an analyzer pass energy of 23.3 eV during spectral acquisition. The takeoff angle of an electron from the sample was fixed at 45° with respect to the specimen surface. The C 1s core-level spectra were decomposed into three Gaussian functions using the IGOR Pro Ver. 5.0 program. For peak synthesis, the full width at half-maximum (FWHM) at 1.7 eV was used for each Gaussian peak.

3. Results and discussion

3.1. Thermal stability in polar matrices

Fig. 1 shows UV–vis absorption spectra of Sp methanol solution (1.0×10^{-5} M) before and after 360 nm light irradiation at ambient temperature. Before light irradiation, main absorption peak of SP-form appeared around at 330 nm. This absorption band was assigned to π–π^* transitions of chromene and indoline rings. Upon light irradiation, the solution changed from colorless to red and a broad absorption band appeared with a maximum at 529 nm. This absorption band was assigned to the PMC-form, which has a zwitterionic structure. After stopping the UV light irradiation, the absorption intensity of the PMC-form gradually decreased over approximately 10 h at ambient temperature.

Fig. 2 shows the time dependence of the absorption intensity of the PMC-form at λ_{max} in methanol (as a polar solution), PVA (as a polar polymer) and in PHPS. The monitored absorption intensity was defined by the centered absorption peak in the visible region, which was generated under UV light irradiation. The absorption peaks of the PMC-form in methanol and PVA were at 529 and 535 nm, respectively. Thermal decay curves of the absorption intensities in methanol and PVA corresponded well to the following single exponential decay function.

$$\ln\left[\frac{A_t - A_\infty}{A_0 - A_\infty}\right] = -kt \qquad (1)$$

where A_∞ is the residual absorbance after long term exposure, A_0 and A_t are the absorbances immediately after UV light irradiation and at any subsequent time t, respectively, and k is the rate constant for the PMC-form to SP-form. According to the conventional approach for evaluation of a first-order reaction, the reaction rate constants, k, and half-lifetimes ($\tau_{1/2}$) of the PMC-form in methanol and PVA were estimated to be 9.6×10^{-5} s^{-1} (7.2×10^3 s) and 3.2×10^{-6} s^{-1} (2.2×10^5 s), respectively. $\tau_{1/2}$ of the PMC-form in PVA was approximately 30-times longer than that in methanol. In the case of the PHPS matrix, the absorption intensity of the PMC-form decreased rapidly within approximately 3 h, because the PMC-form was surrounded by *m*-xylene in the film containing non-polar *m*-xylene at initial state. However the intensity remained constant for 2–3 days after decreasing by approximately half. It is a noteworthy feature that the constant intensity subsequently exhibited a gradual increase from a certain time. The absorption peak shifted to 510 nm after 2–3 days, which suggests that PHPS was completely converted to silica within the 2–3 day period. k and $\tau_{1/2}$ of the PMC-form in PHPS after 2–3 days were estimated to be approximately 8.7×10^{-9} s^{-1} and 8.0×10^7 s, respectively. PHPS would be completely converted into silica within 2–3 days,

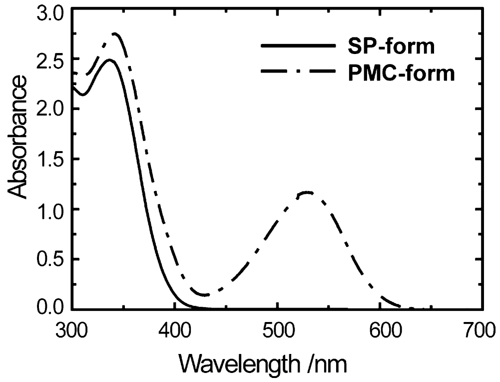

Fig. 1. Absorption spectra of methanol solutions of the SP-form (conc. 1.0×10^{-5} M, solid line) and photostationary PMC-form (broken line) under irradiation with 360 nm light.

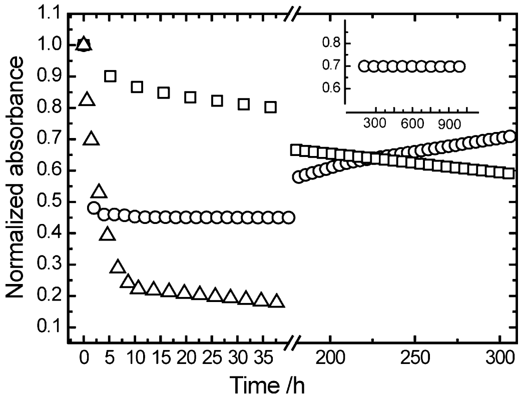

Fig. 2. Time dependence of the normalized absorption intensity at λ_{max} for the PMC-form in various matrices in the dark at 25 °C: (○) silica, (□) PVA and (△) methanol. The inset shows the time dependence of the later time.

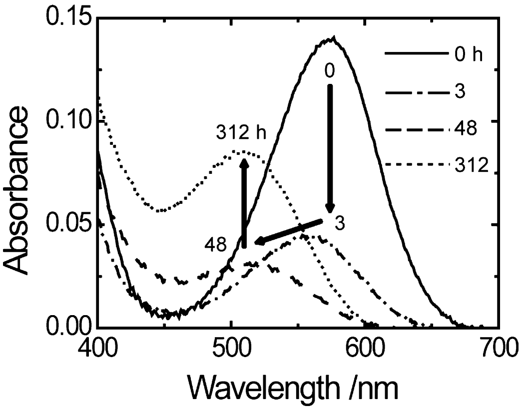

Fig. 3. Time evolution of the absorption behavior of the PMC-form in silica in the dark at ambient temperature.

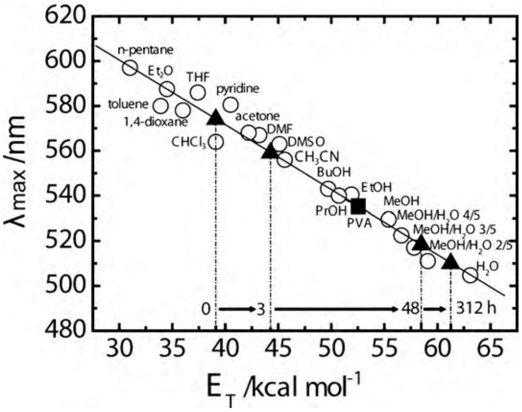

Fig. 4. λ_{max} of the PMC-form vs. E_T: ○ represents experimental; filled symbols represent E_T values that were estimated from the linear fit of the solvents.

the conversion mechanism of which is described later in Section 3.2. $\tau_{1/2}$ for the PMC-form in silica is approximately 10^5 times longer than that in methanol. It is well known that the PMC-form is stabilized in polar solvents and that stability is also significantly enhanced in rigid matrices such as polymer networks [34]. Therefore, a rigid matrix with polar moieties, such as hydroxyl and carboxylic groups, is the best candidate for stabilization of the PMC-form. In a polar medium, the PMC-form is predominantly comprised of charge localized zwitterionic structures that are stabilized in the polar matrix. Nadolski et al. has suggested that the singlet ground state is more polar than the singlet excited state [35]. Therefore, PMC-form is stabilized against external heating in a polar matrix, which results in a short-wavelength shift of λ_{max} (hypsochromic shift) [33,34]. In addition, molecular vibration of the PMC-form in PVA would be strongly restricted due to steric hindrance, so that the probability of cycloreversion is restricted. However, in the case of the silica matrix, another stabilization factor in addition to the matrix polarity and steric hindrance is suggested, due to the significant hypsochromic shift observed.

3.2. *Mechanism of thermal stability*

The absorption spectra of the PMC-form in PHPS following UV irradiation with 360 nm light after dark conditions are shown in Fig. 3. The absorption spectrum before irradiation did not appear in this region. The state just after spin-coating with UV irradiation is denoted as 0 h, where the PMC-form has λ_{max} at 574 nm. λ_{max} decreases with external heating (ambient temperature ca. 298 K) to 559 nm with a slight hypsochromic shift after ca. 3 h. After approximately 48 h, λ_{max} has shifted significantly to 518 nm. It should be noted that the absorption intensity increased with a slight hypsochromic shift to 510 nm after ca. 312 h. These results indicate that the PHPS structure is converted drastically and its structural changing carried out an interaction to PMC-form within the period of 3–48 h. Shimizu et al. and Raymo et al. previously reported the effect of acids on the properties of SPs and observed similar absorption spectrum for SPs in acidic media [36–38]. The unique spectrum was assigned to hydrogen bonding with the PMC-form. Therefore, the band observed at 510 nm can be attributed to the PMC-form with a short conjugated structure, which has interacted with that completely converted to silica. Bleaching of the film was achieved by irradiation with visible light at >420 nm; the visible absorption band had completely disappeared. The spectral changes indicate that the PMC-form returns to the SP-form. However, the film was then kept in the dark and the absorption band at 510 nm slowly reappeared. It was noted that the absorption band centered at 510 nm was formed directly from the SP-form irradiated with 360 nm light after 312 h.

Reichardt introduced the transition energy expressed in kcal/mol in order to explain the solvent effect on λ_{max} for the pyridium-*N*-phenoxide betaine dye in various solvents. This parameter is referred to as the E_T value, which is related to λ_{max} by the following equation [39].

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

Fig. 4 shows a linear plot of λ_{max} for the PMC-form versus E_T parameters in various solvents. E_T for PVA is estimated to be 52.6 kcal/mol from λ_{max} on the straight-line approximation. It is suggested that PVA behaves as a protic polar matrix with similar properties to alcohols (e.g., ethanol or methanol). Each plot of PHPS under conversion is shown as a closed triangle. From λ_{max} of the PMC-form, the E_T values for PHPS under conversion at 0, 3, 48 and 312 h are estimated to be 39.1, 44.3, 58.5 and 61.3 kcal/mol, respectively. These results indicate that the polarity of PHPS is changed from an aprotic nonpolar matrix to a protic polar matrix as the conversion progresses. The unconverted PHPS changed to a tetrasilanol intermediate with similar polarity to that of DMSO within approximately 3 h; however, the tetrasilanol intermediate was very short lived after hydrolysis with water vapor. The intermediate was gradually converted into silica with a similar polarity to that of methanol/water (2/3) within ca. 48 h. PHPS was fully converted into silica polarity similar to that of water within the period of 48–312 h. Therefore, PHPS would be changed to a protic polar matrix with O–H groups having an equivalent polarity to water via the short-lived tetrasilanol intermediate. Fig. 5 shows the IR absorption spectra for PMC-form/PHPS after spin-coating that was measured in the dark over time at ambient temperature. The structure of PHPS in the conversion process and the molecular structure of PHPS with time dependence are also illustrated. The spectrum of the as-prepared film shows several absorptions at 3368, 2937, 2857, 2804, 2165, 1172, 1069, 932 and 829 cm^{-1}. These bands are ascribed to N–H stretching (3368 cm^{-1}), Si–H stretching (2165 cm^{-1}), Si–NH–Si bending (1172 cm^{-1}), Si–N stretching (932 cm^{-1}) and Si–H wagging (829 cm^{-1}) of PHPS, and C–H stretching (2937–2804 cm^{-1}) of the methylene unit of 4-4′-trimethylenbis(1-methylpiperidine) used as catalyst. The absorptions originated from SP appear weakly in the region from 1700 to 1200 cm^{-1}, due to the low concentration. After 3 h, the absorption intensities of Si–H (2165 and 829 cm^{-1}) and Si–NH–Si decrease and an absorption band ascribed to Si–O–Si stretching vibration appears at 1069 cm^{-1}. The absorption intensities of N–H, Si–H, Si–NH–Si and Si–N bands then become weaker and that of Si–O–Si band becomes stronger as time progresses. After

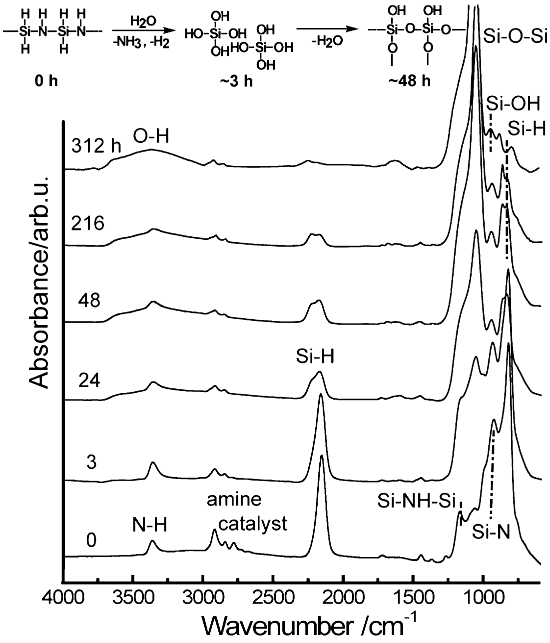

Fig. 5. IR spectra of a film of PHPS with the PMC-form and the molecular structure of PHPS for various times.

312 h, a strong absorption peak of Si–O–Si appears, which indicates that PHPS has been converted to silica by hydrolysis between Si–H and Si–N groups and water vapor, with subsequent cross-linking from condensation reactions. Careful observation reveals that broad and weak bands appear around 3330 and 949 cm^{-1} after 312 h, which are ascribed to O–H and Si–OH stretching vibrations, respectively. It is noteworthy that the FWHM of the absorption peak at 3330 cm^{-1} in the spectrum of the film after 24 h is broader than that of the N–H band, which suggests that this peak is the overlapping of O–H and N–H bands. This would indicate that the O–H group was generated after 24 h. A large amount of the Si–H groups in PHPS have high reactivity with hydroxyl groups. The conversion process from PHPS to silica as determined from the IR analysis is in good agreement with the time-resolved absorption spectra (Fig. 3). The IR features indicate that silica was subsequently formed by condensation and cross-linking reactions of PHPS and the resulting SiO_2 contains residual O–H and Si–OH groups despite complete conversion.

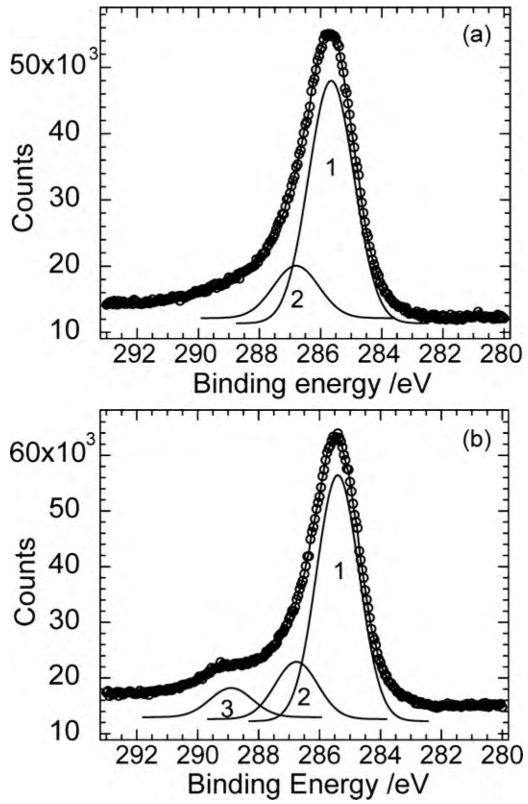

Fig. 6. Decomposition of the C 1s profile for the PMC-form in silica with conversion at (a) 0 and (b) 312 h. The two or three Gaussian components, 1, 2 and 3, correspond to –C–C–, –C–H (285.0 eV), –C–O– (286.2 eV), and –O–C=O (288.5 eV), respectively.

The structural information of the PMC-form was also investigated using XPS. Fig. 6 shows XPS spectra of the PMC-form in silica (0 h) and after complete conversion to silica (312 h), in which a relatively broad C 1s signal revealed the presence of several types of C atoms with small chemical shifts. The signal centered at 285.0 eV originated from (1) –C–C– and –C–H binding energies. This signal was used for calibration of the spectra and was decomposed using the Gaussian method. The best fit of the C 1s spectrum of the PMC-form at 0 h (Fig. 6a) was obtained using two signals corresponding to (1) –C–C and –C–H at 285.0 eV and (2) –C–O at 286.2 eV (1.2 eV shift). However, in the case of the C 1s spectrum at 312 h (Fig. 6b), a third broad signal appears at (3) 288.5 eV (3.5 eV shift) in addition to (1) and (2). The broad signal agrees well with the –O–C=O binding energy, which has been previously reported by several researchers [40–42]. However, the structure of the PMC-form does not contain the –O–C=O group. The third XPS signal is similar to the –O–C=O bond derived from the hydroxyl group of PVA films [43], which are reported as 284.6 and 285.3 eV (0.7 eV shift) and 288.2 eV (3.4 eV shift). As a result, a third chemical bond is assigned to the newly generated hydroxyl group (–C–O–H) with residual O–H and Si–OH in silica. Spectral analysis infers that the structure of the PMC-form has hydrogen bonding between the oxide anion on C–O and the residual O–H and Si–OH in silica; the protonated PMC-form is abbreviated as H···PMC-form. The mechanism for thermal stability and the respective molecular structures, including photographs showing the film states are summarized in Fig. 7. The state of the PMC-form just after photochromic reaction is shown at reaction coordinate 1 (RC-1), which corresponds to 0 h. The absorption spectrum of the RC-1 PMC-form shows λ_{max} centered at 574 nm and the molecular structure has a standard zwitterionic structure. Within approximately 3 h (RC-2), the obtained PMC-form is reverted rapidly to the initial SP-form, because PHPS is mostly in the solution state; however, λ_{max} reaches 559 nm with slight hypsochromic shift and the absorption intensity rapidly decreases. In RC-2, PHPS is converted into the short-lived tetrasilanol intermediate after hydrolysis with water vapor. After 48 h (RC-3), the λ_{max} of the PMC-form at ca. 559 nm undergoes a significant hypsochromic shift to 518 nm and the absorption intensity remains constant. The large spectral shift (RC-2 → RC-3) suggests that the single ground state of the PMC-form (PMC_0) is more polar than the singlet excited state (PMC_1) [44]. The energy gap between PMC_0 and PMC_1 can be widened by differential stabilization with ambient polarity; therefore, the electronic states of these molecular structures have different dipole moments [45]. In RC-3, PHPS is condensed to promote subsequent cross-linking. A small amount of the H···PMC-form is formed from the residual PMC-form by hydrogen bonding with partially uncondensed Si–OH and O–H. After approximately 312 h (RC-4), the H···PMC-form is formed directly from the SP-form, due to protonation with the partially uncondensed Si–OH and O–H in silica. The molecular structure of the H···PMC-form is a protonated zwitterionic structure. In RC-4, the slow coloration indicates a slow open-ring reaction that leads to the formation of the H···PMC-form by protonation. The direct gen-

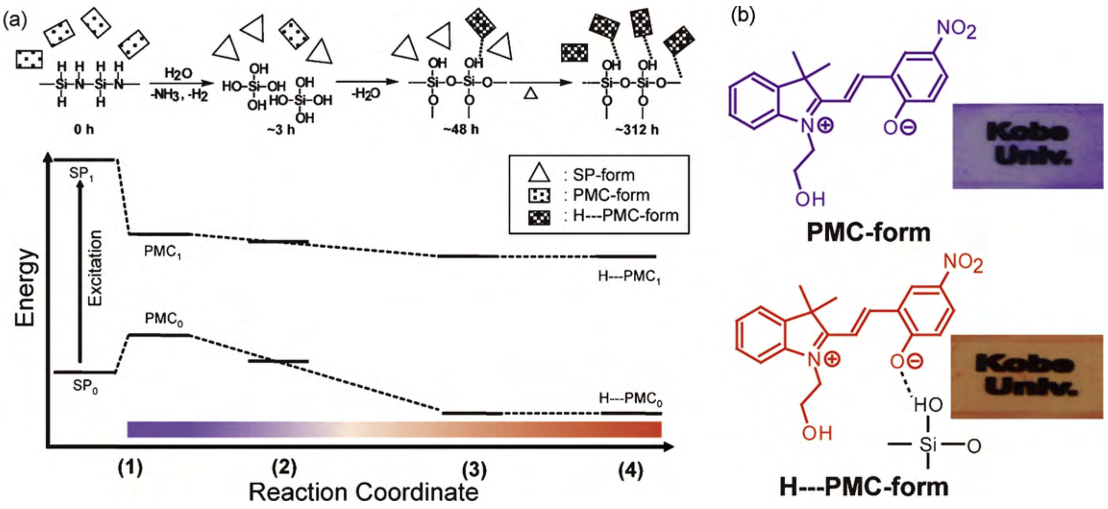

Fig. 7. (a) Schematic representation of the reaction coordinates (RCs) related to the potential energies of the PMC-form and the state of interaction with the PMC-form according to PHPS reaction in the system. The color bar indicates the color tone of the actual film. (b) Molecular structure of the PMC- and H···PMC-forms in a film, and optical photomicrographs of the respective RC-1 and RC-4 states.

eration of the H···PMC-form corresponds to what is referred to as reverse photochromism in RC-4. The increasing absorption intensity (RC-3 → RC-4) is produced directly from the SP-form by reverse photochromism, because the energy gap between H···PMC_0 and H···PMC_1 is wider and stabilized beyond SP_0.

4. Conclusions

After the PMC-form was left in PHPS for approximately 48 h, the λ_{max} of the PMC-form underwent a significant shift from 574 to 518 nm. The IR peaks of Si–H and N–H decreased while the Si–O–Si bands increased, in which indicated the almost complete conversion of PHPS to silica, but with partially uncondensed Si–OH and O–H remaining in the silica. Therefore, it was suggested that after 48 h, the converted silica had a solvent polarity similar to a methanol/water mixture. We have characterized the structure of the PMC-form in silica at 48–312 h and determined a new chemical bond assigned to hydrogen bonding between the oxide anion on C–O and Si–OH in silica. After 48–312 h, the H···PMC-form was also directly generated from the SP-form by protonation with silica. The thermal stability behavior of the PMC-form is suggested as being due to reverse photochromism. From a technological viewpoint, the slow visualization of color change cause by reverse photochromism can be utilized, for example, in time-variable color sensors and hygrometers.

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