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Introduction

Stimuli-responsive organic molecular systems play a significant role in fundamental research and practical applications. Conventional stimuli-responsive molecular systems can be reversibly interconverted between two states by the action of a physical or chemical stimulus such as light,^{1–6} temperature,⁷ chemical,^{8–11} electric field,^{12,13} or mechanical force.^{14–18} These switching molecules exhibit different structures and physicochemical properties in response to external stimuli.

Multi-stimuli-responsive molecular systems have potential applications in future technologies including chemical logic gates,¹⁹ molecular robotics,²⁰ drug delivery,^{21,22} and pharmaco-therapy.^{23,24} However, the development of organic molecules existing in three or more thermodynamically stable states that can

Stepwise structural and fluorescent colour conversion in rhodamine analogues based on light and acid stimulations[†]

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The research and development of multi-stimuli, multi-responsive molecules have attracted considerable attention in chemistry, biology, and material science. Herein, we propose a multi-stimuli-responsive multi-fluorescence system in a single molecule. This system is based on the isomerization that involves ring-opening/ closing reactions of spirolactones of rhodamine analogues (ABPXs), developed by our group, which can be independently controlled by light and chemical stimuli. UV light irradiation opens one of the spirolactones to give thermally stable coloured isomer (\mathbf{Z}) in solution. Detailed synthetic and theoretical investigations reveal that the ring-opening reaction of ABPXs proceeds *via* the formation of a photo-induced charge separated state, followed by the recombination of the biradicals. Furthermore, we explore the structure–kinetic relationships and demonstrate that the introduction of electron-donating substituents into the xanthene ring can tune the lifetime of the photo-generated isomer (\mathbf{D}). These light and chemical input signals can be converted into output signals of distinct colour and fluorescence. The multi-stimuli-responsive multi-colour fluorescence could be distinctively expressed through the combinatorial logic gate.

be manipulated by more than two types of external stimuli in a single molecule is very challenging. A representative work was pioneered by Feringa and co-workers in 2006 (Fig. 1a),²⁵ and such "smart molecules" have witnessed rapid development over the past decades.^{26–34} A promising design strategy to construct this molecular system is the combination of different stimulus-responsive molecules connected through covalent linker groups or assembled within polymers.³⁵ For example, Andréasson *et al.* developed multi-



Fig. 1 Schematic representation of multi-stimuli responsive molecular systems. (a) Bis-tricyclic aromatic enylidenes (BEAs), (b) fulgimide (FG)-dithienylethene (DTE).

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Fig. 2 (a) Structural conversion of rhodamines in response to external stimuli (top) and example of stimuli-responsive rhodamines in previous studies (bottom). (b) Stepwise structural conversions of ABPXs in response to external stimuli.

responsive molecules using different stimuli responses of diarylethene (DTE) and fulgimide (FG) (Fig. 1b).³⁶ Despite the successful use of this design concept, the selective manipulation of coexisting molecular switch units using different types of external stimuli in a single molecule is still limited.

Rhodamines and rhodamine analogues are utilized in many research fields because of their excellent photo-physical and chemical properties.^{37–41} Until now, several rhodamine dyes that respond to light,^{42–44} acid,⁴⁵ redox,⁴⁶ and temperature⁴⁷ through a spiro-ring opening/closing reaction have been developed and are widely used in fluorescence imaging probe,48-54 chemical sensor,^{55–57} molecular memory,⁵⁸ and ink technology (Fig. 2a). More recently, photo-chromic rhodamines have served as fluorescence markers for super-resolution microscopy (photoactivated localization microscopy: PALM) that relies on single-molecule photo-switching.59-61 It has been proposed that the spiro-ring opening reaction occurs, which can lead to the formation of polar nature of Z.44,62 However, the photo-isomerization process of rhodamines has not been clearly elucidated. In this work, we demonstrated the stepwise structural conversion in the rhodamine analogues, namely, aminobenzopyranxanthenes (ABPXs), based on light and chemical stimuli (Fig. 2b). This molecular system is based on the isomerization that involves the ring-opening/closing reaction of spirolactones of ABPXs.^{63,64} During our study on the stimuli-responsive mechanisms of ABPXs (1), we found that a physical stimulus, such as light irradiation, caused the selective opening of one of the two spirolactones. The detailed photoisomerization process of ABPX was investigated by isolating the photo-reaction intermediate. Upon the successive addition of an acid and/or heating, reversible interconversion could be precisely controlled (Fig. 2b). This multi-stimuli-responsive multifluorescence is expressed in a combinatorial logic gate.

Results and discussion

Absorption and fluorescence spectra

To elucidate the photochemistry of the ring-opening/closing reaction of spirolactones, we initially examined the spectral Journal of Materials Chemistry C



Fig. 3 (a) Photo-switching and thermal reversion of spirolactone form (1) to zwitterionic form (1_z). (b) Absorption and (c) fluorescence spectra 40 μ M of 1 in CHCl₃ before (black) and after (red) UV irradiation. The excitation wavelength is 305 nm. Insets show the photographs of 1 in CHCl₃ before and after UV irradiation.

properties of 1 in CHCl₃ by UV/Vis absorption and fluorescence spectroscopy. All measurements were performed at 293 K. The colourless closed form of 1 showed an absorption band in the UV region. Irradiation in the UV region ($\lambda_{irr} = 305 \text{ nm}, t_{irr} = 60 \text{ min},$ xenon lamp) caused a bathochromic shift of absorption band, and a new absorption band appeared in the visible region $(\lambda_{abs} = 510 \text{ nm})$, as shown in Fig. 3b. A clear isosbestic point was observed at 338 nm. Upon UV light irradiation, the solution of 1 gradually changed from colourless to orange, as evident to the naked eye. The vibronic absorption spectrum of the orangecoloured species was almost identical to that of the monocationic species of 1 (see Fig. S1, ESI[†]). On the other hand, no colour change was observed when 1 was dissolved in CHCl₃ previously irradiated with UV light (Fig. S2, ESI†). Upon warming the solution of 1, the absorption at 500 nm decreased and a half-life of 9.1 h ($k = 0.076 \text{ h}^{-1}$) at 298 K (Fig. S3 and kinetics, ESI[†]) was obtained, indicating that the orange-coloured species is reconverted to 1. In addition, 1 showed yellow fluorescence at around 580 nm upon UV irradiation (Fig. 3c).

Photochemistry

These spectral and colour features indicate that 1 isomerizes to a zwitterionic form $(\mathbf{1}_Z)$ by cleavage of one of the C–O bonds in the two spirolactones. Ma and co-workers suggested that $\mathbf{1}_Z$ was produced by the photo-induced ring-opening reaction.⁶⁵ However, the identification of $\mathbf{1}_Z$ was just investigated by the changes of absorption/fluorescence spectra and IR spectra accompanying UV light irradiation. Hence, there is insufficient evidence for the identification of $\mathbf{1}_Z$. Moreover, the elucidation of the photo-chemical reaction mechanism is necessary for the construction of a stimuli-responsive molecular system.

To obtain a strong support for the formation of $\mathbf{1}_z$, we attempted to trap and characterize the zwitterion adducts from the reaction of $\mathbf{1}$ with trimethylsilyl cyanide (TMSCN) in argonpurged CHCl₃ under UV irradiation with reference to the literature.⁶⁶

a)



Scheme 1 Trapping and characterization of (a) photo-generated product (2) by TMSCN, and (b) X-ray crystal structure of 2. ORTEP view of 2 was shown with thermal ellipsoids shown at the 50% probability level.

As expected, the monocyano adduct (2) was obtained in 15% yield, while a substantial amount of 1 was recovered (Scheme 1a). In contrast to UV irradiation, trace amounts of 2 were trapped without UV irradiation under dark conditions. These results indicated the photo-induced spirolactone-ring opening of 1, followed by isomerization to 1_z . The crystal structure of 2 was established by single-crystal X-ray diffraction analysis. The xanthene moiety of 2 adopted a nonplanar distorted conformation. A pair of phenyl rings of 2 was in the *trans* configuration with respect to the xanthene moiety (Scheme 1b). Thus, the CN⁻ addition to 1 caused the inversion of a phenyl ring.

The difference between the ground- and excited-state dipole moments of **1** was then estimated by using Lippert–Mataga and Bilot–Kawski equations and Reichardt's *ENT* solvent polarity parameter (Fig. S9–S11, and Table S1, ESI†).^{67–69} These calculated dipole moments in the excited state were significantly larger than those of the ground state (Fig. 4). Density functional theory (DFT) calculations (CAM-B3LYP/6-31G**) were then carried out to corroborate the experimental results and examine the excited electronic structure. Indeed, the large difference in dipole moment between the S₀ and S₁ states ($\Delta \mu = 9.53$ D) was in good agreement with the experimental results ($\Delta \mu_{AVE} = 10.82$ D), implying that the excited state is more polarized than the ground state. The optimized



Fig. 4 DFT calculations of 1 in the S_0 and S_1 states at the CAM-B3LYP/6-31G** level. Left panels: Electrostatic potential (ESP) distribution. Middle panels: Optimized geometry. Right panels: Ground- and excited-state dipole moments.

geometry and electrostatic potential (ESP) distribution of **1** are shown in Fig. 4. The two phthalide moieties of **1** were orthogonally arranged relative to the xanthene moiety in the S₀ state, which is in good accordance with the results of previous X-ray crystallographic analysis (Fig. S4 and S5, ESI†). The charge separation (CS) between the phthalide moiety and the diethyl aniline moiety in the S₁ state was larger than that in the case of the planar xanthene structure in the S₀ state, which might be due to the asymmetric distorted xanthene structure. This type of photo-induced CS state is often observed in the spirolactone form of triarylmethanes or rhodamines with nearly perpendicular donor–acceptor orientation.^{70,71} These calculations indicated that the charge-separated structure (**1**_{CS}*) is formed in the excited state.

Mechanistic investigations were further performed for a better understanding of the photo-chemical reaction of **1**. The ¹H NMR spectrum of **1** in argon-purged CDCl₃ was recorded after UV irradiation at room temperature. The ¹H NMR spectrum showed severe line broadening with prolonged light irradiation and the solution of **1** gave no resonance signals corresponding to the xanthene protons (H_c – H_g) after 60 min of irradiation (Fig. S6, ESI[†]).

From the ¹H NMR spectral behaviour, it is assumed that the photoisomerization from 1 to 1_z proceeds *via* the formation of a radical intermediate. Based on the hypothesis, the EPR spectrum of 1 was measured in argon-purged CHCl₃ after UV light irradiation at room temperature, but no EPR signals were observed. This result indicated that the radical intermediate is unstable at room temperature. Therefore, we isolated the isopropyl-cyano-radical-trapped adduct 3 from the photochemical reaction of 1 with azobisisobutyronitrile (AIBN), a typical radical initiator, in argon-purged 1,2-dichloroethane (DCE) at room temperature (Scheme 2a). By contrast, any cyano isopropyl radical adducts were not obtained upon heating. Further structural characterization of 3 by X-ray crystallographic analysis revealed that the radical derived from the



Scheme 2 Trapping and characterization of (a) photo-generated product (3) by AIBN, and (b) X-ray crystal structure of 3. ORTEP view of 3 was shown with thermal ellipsoids shown at the 50% probability level. (c) Photo-generated products (4 and 5) by styrene.



Fig. 5 Plausible mechanism underlying the photo-chemical reaction of **1**. CS: charge separation.

C-O bond cleavage of the spirolactone in **1** attacks the isopropyl cyano radical. It is noteworthy that UV absorption of **1** in degassed styrene solution led to a radical reaction that gave styrene-inserted compounds **4** and **5** (stereochemistries were not determined), supporting the formation of a bi-radical intermediate (Scheme 2b).

From the experimental and computational studies, a plausible mechanism for the photo-chemical reaction of **1** is proposed, as illustrated in Fig. 5. Upon the absorption of UV light, intramolecular charge transfer from the diethyl aniline moiety to the phthalide moiety in **1** occurs to form $\mathbf{1}_{CS}^*$ in the excited state. Then, $\mathbf{1}_{CS}^*$ is rapidly converted to bi-radical species **6** after C–O bond cleavage in one of the spirolactone-rings. This selective photo-chromic reaction (opening of one spirolactone) might be triggered from the asymmetrically distorted structure of $\mathbf{1}_{CS}^*$. Compound **6** subsequently undergoes recombination of the bi-radicals to afford the coloured $\mathbf{1}_Z$ in the ground state. Alternately, homolytic C–O bond cleavage is likely to occur, to give bi-radical species 7, indicating that the photo-chemical reaction of **1** proceeds *via* several radical pathways.

Structure-kinetic relationship

We next synthesized ABPX derivatives 8, 9, 11, and 14 with different electron-donating amino substituents, in agreement with the Hammett σ^+ constants, as proposed by Mayr and co-workers,72 and explored the structure-kinetic relationship of the photo-generated zwitterionic isomer (Fig. 6a). Compounds 8 and 9 were synthesized according to the previous research methods.⁷³ Compounds 11 and 14 could be synthesized from the corresponding benzophenone derivatives (Fig. 6b). The closed forms of these derivatives were isomerized into the open forms 8z, 9_{7_2} 11_{7_2} and 14_{7_2} in CHCl₃ under continuous UV light irradiation (Fig. S14, ESI[†]). The absorbance of the open forms decayed in CHCl₃ in the temperature range 298 to 313 K over 8 h (Fig. S15, ESI[†]). The thermal bleaching of these isomers followed first-order kinetics (Fig. S16 and Table S3, ESI⁺). The reaction rate constant (k) obtained from the first-order time plots was small, as σ^+ had a large negative value. An excellent linear relationship was obtained in the single regression of k_{313K} for the value of σ^+ (Fig. 7). However, there was no correlation between the activation



Fig. 6 (a) Photo-switching and thermal reversion of ABPXs **8**, **9**, **11**, and **14** with different electron-donating amino substituents. Hammett σ^+ constants of electron-donating substituents proposed by Mayer and co-workers are described.⁷² (b) Synthesis of **11** and **14**. Reagents and conditions: (i) phthalic anhydride, toluene, reflux, 24 h. (ii) resorcinol, CH₃SO₃H, 110 °C, 6 h.



Fig. 7 Correlation between the first-order kinetic rate constant (k_{313K}) and Hammett constants σ^+ of different electron-donating amino substituents for ABPXs. The coloured characters show the half-lives of the ABPXs.

parameters obtained from the Eyring plots and the σ^+ value (Table S4, ESI⁺). From these results, it is concluded that the introduction of an electron-donating amino substituent enhances the stability of the xanthylium cation and tunes the lifetime of the ring-opened state. As opposed to other reported zwitterionic form of rhodamines, the ABPX family has the advantage of photochromic features with a long lifetime ($t_{1/2}$ = 4.1–8.6 h).

Molecular logic gate

Based on the result of photo-reaction of ABPXs, the acid activated switching was further studied by UV/Vis spectroscopy. For this purpose, CHCl₃/MeOH solvent mixtures were employed

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Fig. 8 (a) Schematic illustration and (b) fluorescence spectra of three states ($\mathbf{1}$, $\mathbf{1}_{z}$ and $\mathbf{1}_{D}$). The excitation wavelength is 365 nm. (c) Truth table and (d) logic gate diagram for multi-stimuli responsive multi-colour fluorescence system.

because it was found that the photo-isomerization from 1 to $\mathbf{1}_{\mathbf{Z}}$ was accelerated by the addition of small amounts of MeOH to CHCl₃ solution (Fig. S7, ESI[†]). Upon light irradiation, photoswitching of 1 was consistently observed in 1.0% MeOH/CHCl₃ solution to generate the orange-coloured $\mathbf{1}_{\mathbf{Z}}$. To our delight, the addition of trifluoroacetic acid (TFA) caused a further bathochromic shift of absorption band, and an absorption band appeared at approximately 550 nm and 590 nm, which was attributed to the dicationic species ($\mathbf{1}_{\mathbf{D}}$). The solution drastically changed from orange to purple in chemical-stimulated interconversions (Fig. S8, ESI[†]).

We finally applied this unique multi-stimuli responsive multi-colour fluorescence system to the combinational logic gates. This molecular logic gate consists of two physical/chemical inputs and three different fluorescent outputs (Output 1, 2 and 3 for emissions at 515 nm, 580 nm, and 630 nm, respectively) and functions without complicated arithmetic operations (Fig. 8). The physical and chemical inputs were defined as UV light irradiation (305 nm) and 1.0 eq. of TFA in 1.0% MeOH/CHCl₃ solution. Naked-eye observation of 1 showed that the initial state (0, 0) was blue-green in fluorescence colour (Output 1) *via* a NOR logic gate. As it can be seen from the truth table, this blue-green fluorescent solution was changed to yellow fluorescent solution (Output 2) upon UV irradiation (1, 0). The photo-input followed by chemical-input operations (1, 1) further caused the fluorescence colour change from yellow to orange (Output 3).

Conclusions

We have demonstrated a light- and chemical-responsive molecular system based on the isomerization that involves the ring-opening/closing reaction of spirolactones of aminobenzopyranxanthenes (ABPXs). UV light irradiation selectively opens one of the spirolactones to give a stable and long-lived isomer. We also obtained a comprehensive reaction mechanism of the photo-induced spirolactone-ring cleavage by employing a combination of experimental and computational approaches. Chemical stimulation by an acid allows the photo-generated form to be further isomerized to the thermally stable form. The solution changes from colourless to orange and then to purple. On the other hand, the photo-responsive and chemically responsive coloured species can be reverted to the closed isomer form by a thermal back-reaction. It is noteworthy that three states of the multi-stimuli responsive multi-colour fluorescence switching could be expressed through the combinatorial logic gate. We believe that the multi-stimuli responsive molecular system developed in this study offers a new perspective for various technologies applying molecular switching.

Conflicts of interest

There were no conflicts to declare.

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