

Solid-State Photoinduced Luminescence Switch for Advanced Anticounterfeiting and Super-Resolution Imaging Applications

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Supporting Information

ABSTRACT: Solid-state organic photoswitches with reversible luminescence modulation property are highly attractive because of their wide prospects in advanced photonic applications, such as optical data storage, anticounterfeiting and bioimaging. Yet, developing such materials has long been a significant challenge. In this work, we construct an efficient solid-state photoswitch based on a spiropyran-functionalized distyrylanthracene derivative (DSA-2SP) that exhibits exceptional reversible absorption/luminescence modulation ability. Efficient photoswitching between DSA-2SP and its photoisomer DSA-2MC are facilitated by large free volumes induced by nonplanar molecular structures of DSA moieties, as well as the intramolecular hydrogen bonds between the DSA and MC moieties. Consequently, the excellent solid-state photochromic property of DSA-2SP is highly applicable as both anticounterfeiting inks and super-resolution imaging agents.

Spiropyran (SP) and its derivatives represent one important class of photochromic molecules, and have attracted considerable research interest for their versatile applications as data storage medium,^{1–3} chemical sensors,^{4,5} biological imaging agents,^{6–10} and other functional materials.^{11–17} These molecules exhibit distinct absorption and luminescence spectral changes under ultraviolet radiation, as they experience structural isomerization from the unconjugated SP form to conjugated merocyanine (MC) form.¹⁸ In the past few decades, covalently attaching SP to other fluorophores has led to the remarkable development of many multicolor photoinduced luminescence switches.^{19,20} However, most of these switches function only in the solution phase. Developing efficient solid-state luminescence switches remains significantly challenging and at the same time increasingly imperative for numerous applications.²¹

To this end, Yu et al. reported that two cationic microcrystalline pyrido-spiropyrans exhibited photochromism in the crystalline state.²² This solid-state photoswitching is attributed to the presence of a strong electron-withdrawing group (methylpyridinium) and the possible “dilution effect” of

iodide anions. However, the methylpyridinium group and the iodide anion could also quench the emission of this compound in the crystalline state. Harada et al. showed that decreasing temperature to 80 K enhanced the photochromism of SP in the solid state.²³ This enhancement is due to slowing down the reaction rate of MC to SP photoisomerization. Nevertheless, such a low temperature limits its practical applications.

In fact, the primary challenge in the solid-state photo-switching of SP molecules concerns tight molecular packing in aggregated molecules. Such tight molecular packing significantly impedes the cis–trans transformation, which occurs during photochemical reactions between the SP and MC forms. Consequently, providing a large free volume in the solid state is crucial to facilitate efficient photoswitching. Recently, highly twisted π -conjugated luminescent molecules have attracted substantial research interest for their outstanding fluorescence quantum yield in the solid state. Their highly three-dimensional structures avoid strong intermolecular π – π stacking and lead to a unique phenomenon of aggregation-induced-emission (AIE).²⁴ Moreover, the nonplanar conformations of AIE molecules often lead to a loose packing in the solid state. We thus reason that linking a highly sterically bulky AIE molecule to SP could provide considerable free volume, thus facilitating efficient SP–MC photoisomerization.

Inspired by this design strategy, we covalently linked two SP moieties to a popular AIE molecule, 9,10-distyrylanthracene (DSA), resulting in a novel photochromic compound (DSA-2SP, Figure 1a). DSA-2SP exhibits highly efficient and reversible solid-state luminescence switching under alternating UV light and heat/visible light treatment. Moreover, it also emits bright fluorescence. Accordingly, we have successfully demonstrated its application in both optical anticounterfeiting and super-resolution imaging.

We first synthesized DSA-2SP using SP-COOH and DSA-2OH via esterification reaction (Schemes S1–S3), and studied its photoswitching characteristics in the solution phase. Before UV irradiation, DSA-2SP dissolved in tetrahydrofuran (THF) showed a strong absorption peaked at 410 nm and an emission centered at 550 nm (Figure S1b,c), which are attributed to the

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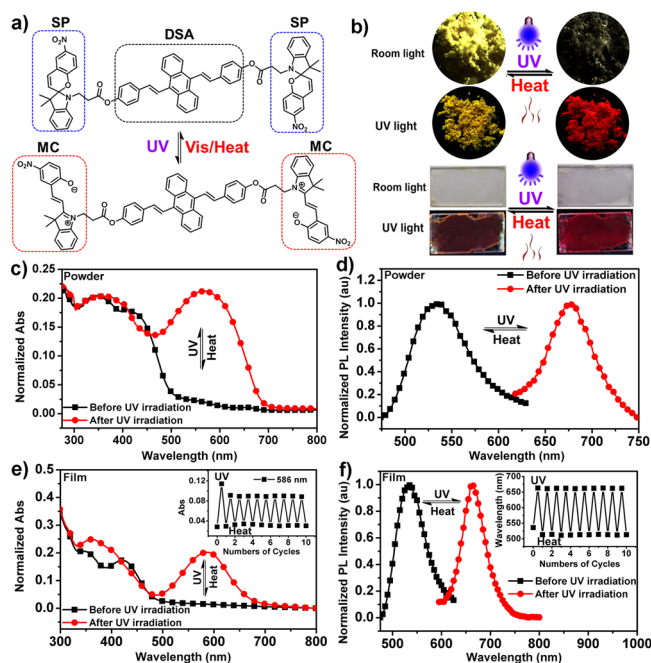


Figure 1. (a) Reversible structural isomerization between DSA-2SP and DSA-2MC under different stimuli. (b) Visible and fluorescent pictures of DSA-2SP powders and films. (c) UV-vis reflection and (d) PL spectra of DSA-2SP powders before and after UV irradiation, ex: 410 and 560 nm. (e) UV-vis absorption and (f) PL spectra of a spin-coated DSA-2SP film before and after UV irradiation, ex: 410 and 560 nm. Insets of panels e and f: reversible switching of the absorption and emission by the UV-Heat cycle.

DSA moiety. Upon continuous 365 nm UV light irradiation, DSA-2SP exhibited a noticeable change in both its visual color (from colorless to cyan) and fluorescence (from yellow to orange). Accordingly, a new absorption band (maximized at 590 nm) and a corresponding emission band (centered at 630 nm) started to emerge and gradually intensified (Figure S1b,d). These new absorption and emission bands are consistent with those of the MC moieties which possess a more extended π -conjugation than their SP isomers, thereby indicating the photoswitching from SP to MC moieties. It is noteworthy that

MC isomers are unstable in THF and their colors fade off within 20 s after UV light was turned off (Figure S2a). Such rapid switching from MC to SP isomers is due to strong vibrational and rotational freedom of DSA-2SP in the solution phase.

The successful photoswitching of DSA-2SP in THF solution motivated us to explore its photochromic behaviors in the solid-state. It was exciting to discover that the solid powder of DSA-2SP exhibited efficient photoswitching at room temperature, under the irradiation of a hand-held ultraviolet lamp (365 nm). We noticed that after UV exposure, the color of the DSA-2SP powder immediately changed from yellow to dark purple (Figure 1b). At the same time, a new UV-vis absorption band centered at 590 nm and an emission band peaked at 670 nm appeared, corroborating the photoswitching from SP to MC moiety (Figure 1c,d; detailed dynamic studies of these absorption and emission changes are available in Figures S3 and S4). Moreover, the UV exposed DSA-2SP could be restored after brief heating at 90 °C for 5 min. The fluorescence quantum efficiencies of the DSA-2SP powders through 10 cycles of UV-Heat switching are shown in Figure S5.

Similar to the spectral changes in its powders, both the absorption and emission bands of DSA-2SP thin film demonstrate reversible changes under alternated UV irradiations and heat treatment (Figure 1e,f). Multiple cycles of such treatment indicate efficient reversibility and antifatigue capability of DSA-2SP. We also found that upon photo-switching, DSA-2MC in the thin film exhibit much improved stability than that in the solution phase. For example, its color could be retained for >24 h in a dark room at ambient temperature without much fading (Figure S2b). Similar characteristics are also found in DSA-2SP doped PMMA films (Figure S6).

Powder X-ray diffraction (PXRD) experiments on pristine DSA-2SP powder showed no obvious diffraction peaks, suggesting that the solid DSA-2SP stay in an amorphous state and lack close molecular packing (Figure 2a). Moreover, X-ray photoelectron spectroscopy (XPS) experiments on DSA-2SP thin film reveal a noticeable increase in binding energy of nitrogen 1s electron after UV irradiation (Figure 2b). This increase in binding energy could be understood by considering that as UV irradiation convert SP to MC moiety, the positively

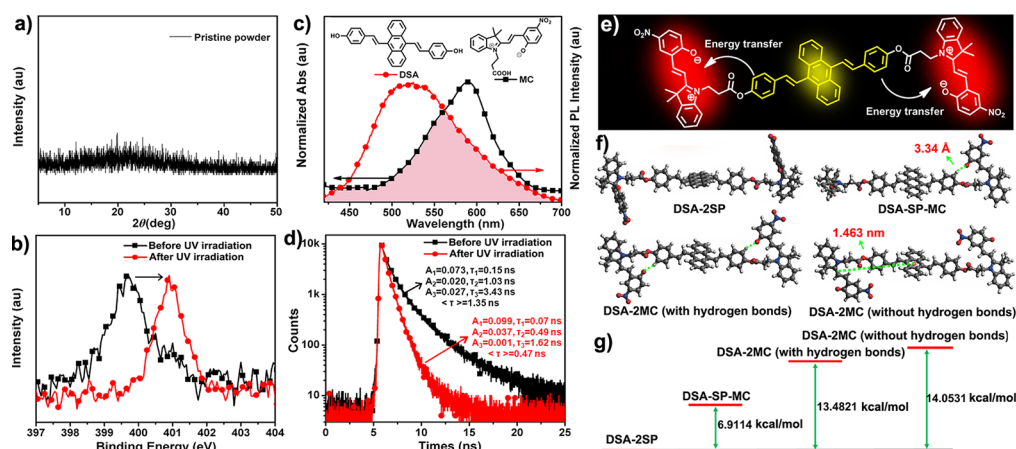


Figure 2. (a) PXRD pattern of the pristine DSA-2SP powder. (b) XPS spectra of DSA-2SP film before and after 365 nm UV irradiations. (c) Overlap of MC Absorption and DSA emission spectra, ex: 410 nm. (d) Fluorescence decays of DSA-2SP film before and after 365 nm UV irradiations. (e) Mechanism of photochromic luminescence of DSA-2SP under UV irradiations. (f) Optimized molecular structures of various conformations and (g) their relative enthalpy levels.

charged indoline cation in the zwitterionic MC moiety render it more difficult to extract the nitrogen 1s electrons. We also noticed that the absorption band of MC substantially overlapped with the emission band of DSA (Figure 2c), while the distance between these two moieties was only ~ 1.463 nm (Figure S7). Consequently, there exists considerable intramolecular energy transfer from DSA to MC moieties (Figure 2e). Indeed, after UV irradiations, the average fluorescence lifetime of DSA-2SP thin film at 530 nm (emissions from the DSA moieties) exhibits a significant decrease from 1.35 to 0.47 ns (Figure 2d), suggesting significant energy transfer to the MC moieties.²⁵ The energy transfer process from the DSA donor to the MC acceptor was further demonstrated by the PL excitation spectra (Figure S8) and ultrafast transient absorption spectra (Figure S9).

To gain further insights into the photochromic behaviors of DSA-2SP, we performed quantum chemical calculations based on the density functional theory (DFT). Our DFT calculations show that the DSA group possesses a highly nonplanar molecular structure (Figure 2f). Such a steric structure could afford significant free volume in the DSA-2SP powder, thus enabling efficient photoisomerization from the SP to the MC moieties in the solid-state. We also noticed that upon photoisomerization, hydrogen bonding interactions between the MC and DSA moieties in the resulted DSA-2MC were present (CH $\cdots$ O distance: ~ 3.34 Å; Figure 2f). These hydrogen bond interactions further stabilize the MC form by ~ 0.57 kcal/mol, leading to more efficient photoswitching from the SP to MC (Figure 2g). Moreover, this enhanced stability endows the MC form a longer lifetime after UV is turned off. Indeed, our calculations reveal that the energy differences between the SP and MC forms is reduced to ~ 6.91 kcal/mol, in comparison to ~ 14.9 kcal/mol in a reference compound SP⁰/MC⁰.²⁶ All these factors, including the relative stabilization of DSA-2MC with respect to DSC-2SP and the availability of large free volumes in the solid-state enables efficient photoswitching in DSC-2SP.

The excellent photochromic property of DSC-2SP was demonstrated in its applications as an anticounterfeit ink. Consequently, we printed an umbrella onto a filter paper with DSA-2SP solution (Figure 3). After a complete drying under ambient conditions, we observed a pale yellow pattern on the paper (Figure 3a). The light color and the associated low background interference suggest that DSA-2SP is a suitable anticounterfeit ink. Next, exposing the printed paper to 365 nm UV light immediately changed the visible color of the umbrella dye to blue violet (Figure 3b and Video). This color change is easily distinguishable by a naked eye. Furthermore, the visible color of the printed pattern was restored to its initial state after heating at 90 °C for 1 min. This color reversibility was reproduced for many cycles without fail (Figure 3e). Finally, the corresponding fluorescence changes between bright yellow to red emissions provided even higher contrast and clearer signals than the visual colors of DSA-2SP during this process (Figure 3c,d).

We would like to point out that DSA-2SP has a large molecular weight (>1000) and is highly difficult to crystallize. These properties render it extremely challenging to characterize the molecular structure of DSA-2SP. The potential security features and excellent solid-state photochromic properties of DSA-2SP make it a promising anticounterfeit ink with either visual color or emission changes.

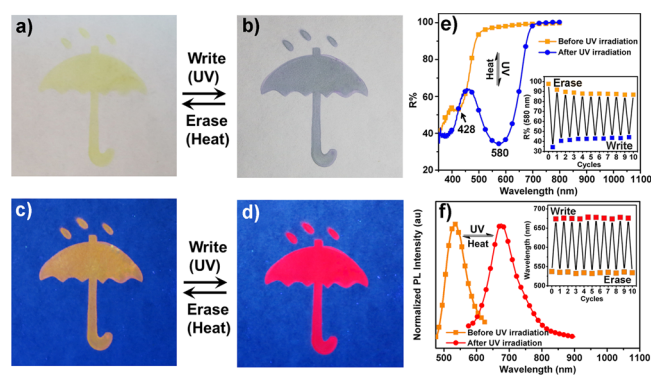


Figure 3. Illustration of DSA-2SP as an anticounterfeiting ink on a filter paper printed with an umbrella-shape. The printed images taken (a) under visible light and (b) after 1 min UV irradiation, and their corresponding fluorescent images in panels c and d. (e) The reflective UV-vis spectra and (f) corresponding PL spectra of the filter paper printed with DSA-2SP before and after 365 nm UV irradiation, respectively. Insets: (e) a plot of the reflectance at 580 nm; (f) switches of the peak emission wavelength through 10 cycles of UV-writing and heat-erasing at 90 °C.

The photoswitching characteristics of DSA-2SP also endow it with a substantial potential in super-resolution imaging. In many super-resolution imaging techniques such as stochastic optical reconstruction microscopy (STORM)²⁷ and photo-activated localization microscopy (PALM),²⁸ photoswitchable fluorophores play a key role for achieving good imaging quality. To demonstrate the application of DSA-2SP in super-resolution imaging, we uniformly doped this compound in the diblock copolymer of polystyrene-*block*-poly(ethylene oxide) (PSt-*b*-PEO). The amphiphilic nature of PSt-*b*-PEO leads to self-assembly of water-dispersed cylindrical micelles in aqueous solution (Figure 4a; see Supporting Information for detailed preparation process). In these cylindrical micelle nanostructures, continuous 302 nm ultraviolet light (~ 0.40 mW/cm²) and intermittent 561 nm laser (~ 525.7 mW/cm²) irradiations enabled the on/off switching of red fluorescence (from the fluorescent MC moiety and nonfluorescent SP moiety of DSA-2SP, respectively), and permitted the reconstruction of super-

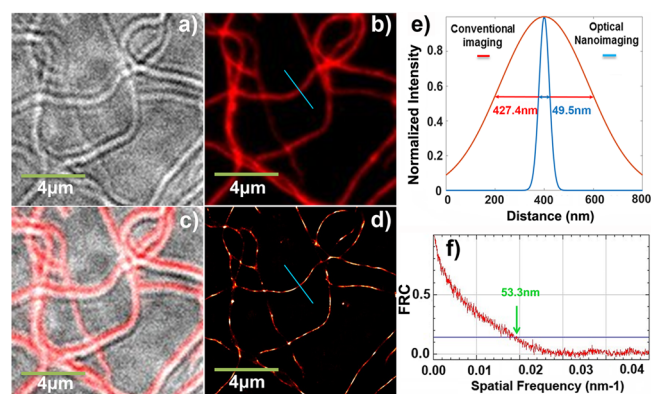


Figure 4. Super-resolution imaging of cylindrical micelles formed from PSt-*b*-PEO copolymer self-assembly staining by DSA-2SP. (a) Bright field image. (b) Conventional fluorescence image. (c) Merged bright field and fluorescence image. (d) Super-resolution imaging corresponding to the same field of fluorescence image. (e) Fluorescence cross-sectional profiles of single cylindrical micelle. (f) Fourier ring correlation (FRC) curve calculated from panel d.

resolution images (Figure S10). Our results showed that the super-resolution image of PSt-*b*-PEO cylindrical micelles exhibited greatly enhanced resolution compared to conventional fluorescence image (Figure 4 and Figure S11). Per Gaussian deconvolution, the full-width at half-maximum (fwhm) of a fluorescent micelle is ~ 49.5 nm in the super-resolution imaging mode, cf. ~ 427.4 nm in the conventional fluorescence imaging mode (Figure 4e). During our experiment, the overall STORM resolution of the super-resolution image amounts to $\sim 53.3 \pm 0.42$ nm, as calculated from the Fourier ring correlation (FRC) curve (Figure 4f).

In summary, we report a highly efficient photochromic spiropyran-functionalized distyrylanthracene derivative, DSA-2SP, which photoswitching in both absorption and fluorescence of DSA-2SP is highly reversible under alternating UV and visible light treatment. Notably, such switching is very efficient not only in the solution-state but also in the solid-state (such as in solid powders and films). We showed that the efficient photoswitching between DSA-2SP and DSA-2MC are facilitated by large free volumes induced by nonplanar molecular structures of DSA moieties, as well as the intramolecular hydrogen bond interactions between the DSA and MC moieties. Finally, we successfully demonstrated the application of DSA-2SP as an anticounterfeit ink, and as super-resolution imaging agent. We postulate that these results have significant implications for developing advanced solid-state photochromic materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b07738.

Synthesis and characterizations, UV-vis and PL spectra, dynamic studies, transient absorption, super-resolution imaging, fluorescence quantum efficiency (PDF)

Video of exposing printed paper to 365 nm UV light (AVI)

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Notes

The authors declare no competing financial interest.

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