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Photoactivatable Aggregation-induced Emission of Triphenylmethanol

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Triphenylmethanol (TPOH) is a non-fluorescent compound. Interestingly, after UV irradiation at 254 nm, TPOH showed strong blue fluorescence on solid surface. Moreover, the fluorescence can be quenched by UV irradiation at 365 nm, making the photoactivatable fluorescence reversible. TPOH is thus applied for rewritable photopatterning tuned by UV light.

Photoactivatable fluorophores¹ undergo fluorescent switches upon light irradiation, which are attracting materials for a broad range of applications in chemistry,^{2, 3} materials⁴ and biosensing.5, 6 Conventional fluorescent molecules, such as rhodamine^{7, 8} and fluorescein,^{9, 10} encounter aggregationcaused quenching (ACQ), so that photoactivatable fluorophores based on them are usually not suitable for use in aggregate or solid state. To address this challenge, fluorophores with aggregation-induced emission (AIE) characteristics¹¹⁻¹³ display weak fluorescence when dissolved in solvent but are strongly fluorescent in aggregates, making them highly efficient solid-state fluorophores.¹⁴⁻¹⁹ Taking advantage of this property, photoactivatable AIE fluorophores based on tetraphenyl ethylene (TPE)²⁰ and salicylaldehyde hydrazine (SA)²¹ derivatives have been developed by Tang's group and our group, respectively, which showed strong fluorescence in aggregates and solids upon irradiation by UV light. Nevertheless, because the mechanism of photoactivation for these designs are based on photolabile groups,²² the photoactivatable AIE fluorescence is not reversible, hindering their potential application as solid materials with rewritable fluorescence.

Triphenylmethane derivatives are members of traditional dyes with bright colors.²³⁻²⁵ Their switch between the triphenylmethane and tritylium forms upon UV irradiation at 254 nm leads to the well-known photochromism

characteristics of these triphenylmethane dyes. The color changes from leuco state to colored state because of the red shift of absorption spectrum when triphenylmethane becomes tritylium.^{26, 27} Early studies demonstrated that the fluorescence of some tritylium molecules in common solvents at low viscosity was very weak,^{28, 29} while stronger fluorescence was observed in highly viscous media (or at low temperature).³⁰⁻³² These findings indicated the tritylium molecules might have AIE-like characteristics, thus we thought tritylium-generating triphenylmethane derivatives, such as triphenylmethanol (TPOH), could be ideal photoactivatable AIE flurophores. One key feature for the photo-induced transformation between tritylium cation (TPM⁺) and TPOH could be reversibility, therefore the photoactivatable AIE fluorescence of TPOH, if present, might be reversible as well.



Fig 1 (a) Photographic images of TPOH luminescence on silica surface under UV1 and UV2 irradiation. Visualization of fluorescence was by a flash excitation at 365 nm within 10 seconds to avoid irradiation effect. (b)Photographic images of TPOH on silica surface before and after UV1 irradiation. (c) Schematic diagram of the photoactivation reaction on silica surface.

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In this work, we found that TPOH was nonfluorescent but subsequently emitted strong fluorescence in aggregate state or on solid surface after irradiation by UV light at 254 nm (UV1). Interestingly, the photo-induced fluorescence of TPOH was quenched when irradiated by UV light at a longer wavelength of 365 nm (UV2), and further repeatable on and off by UV1 and UV2, respectively. The mechanism of the photoactivatable AIE fluorescence was then studied, and such property of TPOH was also applied for rewritable photopatterning.

A visible image of the photoactivatable fluorescence of TPOH on solid surface of silica was shown in Figure 1a. TPOH was initially nonfluorescent. After UV irradiation at 254 nm (UV1) for 5 min, strong photoactivatable fluorescence was observed. Indeed, the TPOH spot on silica also changed from colorless to slightly yellow upon UV1 irradiation (Figure 1b). The yellowish color was the characteristic color of tritylium cation, suggesting the photo-induced generation of tritylium might be responsible for the photoactivatable fluorescence. Interestingly, when the fluorescent state of activated TPOH was placed under UV irradiation at 365 nm (UV2) for a longer time (30 min), the fluorescence was quenched. Subsequently, the fluorescence could be recovered and quenched again by UV1 and UV2 irradiation, respectively (Figure S1, Supporting Information). The reversible activation and deactivation of fluorescence at solid surface could be repeatable for at least 5 times (Figure S2).

To investigate the origin of TPOH's photoactivatable fluorescence, we carried out the study in solvents. As shown in Figure 2a and 2b, TPOH completely dissolved in acetonitrile (1% water fraction) and showed very weak fluorescence even after UV1 irradiation, in contrast to its fluorescence enhancement on solid surface (Figure 1a). With increasing amounts of water fraction, the photoactivatable fluorescence enhanced to its maximum at 60% water. Further addition of water to the solvent to 70% or above caused severe cloudy and precipitation, making the apparent fluorescence intensity decreased. Photoactivation was essential for the fluorescence to occur in



Fig 2 (a) Fluorescent spectra of TPOH in acetonitrile with different water fractions (fw%). (b) Fluorescent intensity at λ =381 nm with different water volume fractions. For



more clear photos, see Figure S3. (c) fw% = 1 and 60 before and after UV1 irradiation. See Figure S4 and S5 for excitation spectra and photoactivation kinetics for fw% = 60

Fig 3 Partial ¹H NMR spectrum (1 mM solution in acetonitrile- d_3 with 1% D₂O) of triphenylmathanol (TPOH), Triphenylcarbenium tetrafluoroborate (TPM^{*}) and TPOH after UV1 irradiate for 1.5 h.

60% water, but giving little fluorescence in 1% water (Figure 2c). Dynamic light scattering (DLS) result showed that insoluble particles with an average diameter of around 202 nm were formed in 60% water (Figure 2d). These results suggested the presence on solid surface or aggregates in solution, instead of freely dissolved, was critical for the photoactivatable fluorescence of TPOH.

We hypothesized that the reason for this phenomenon was likely because of two factors: (1) the tritylium cation (TPM⁺) formed after UV irradiation of TPOH was not very stable when dissolved in solvent containing trace water or the leaving OH⁻, so that the half-life of TPM⁺ was sufficiently long only when the molecule was on the solid surface or in the aggregates of TPOH suspended in poor solvent; (2) even if TPM⁺ could be stable in good solvent, its fluorescence might still be quenched by the intramolecular rotations of phenyl moieties connected by C-C single bonds.

To support our hypothesis, first, we studied the ¹H NMR spectrum of TPOH before and after UV1 irradiation, as well as a TPM⁺ salt (tritylium tetrafluoroborate) in acetonitrile- d_3 containing 1% D₂O. Three nearly identical spectra with neglectable difference in chemical shifts and relative intensity of the peaks were collected for the above three samples (Figure 3), indicating TPM⁺, either formed by UV1 irradiation or originated from salt, transformed into TPOH in good solvent within the time scale for our NMR sample preparation (~15 min). Then, the fluorescence of TPM⁺ salt in anhydrous acetonitrile with different amounts of glycerin were measured. We assumed that TPM⁺ should be sufficiently stable in anhydrous acetonitrile during our measurement. In this case, with more glycerin in the solvent to increase the viscosity of the solution, the fluorescence of "TPM⁺" was enhanced accordingly (Figure S6). This is a characteristic dependence

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between fluorescence and viscosity for typical AIE fluorophores.

To prove the formation of TPM^+ from TPOH after UV1 irradiation, we then measured the ESI-MS (positive ion mode)

spectra of TPOH in methanol before and after UV1 irradiation. As shown in Figure S7, for TPOH in methanol without UV1 irrad-



Fig 4 (a) Rewritable photopatterning materials for printing the word "CHEMISTRY" (b) "Face changing" between UV1 and UV2 irradiation

iation, a sole peak of m/z = 243.1 (TPM⁺) was observed. This was normal, because even for a TPOH solution without any TPM⁺, TPM⁺ signal was usually dominant in ESI due to the ease of OH⁻ leaving under the ionization condition. However, for TPOH in methanol after UV1 irradiation for 1.5 h, another peak of TPOMe ([M+H]⁺ = 275.1) was present, indicating the exchange between TPOH and TPOMe in methanol occurred only under UV light, which was very likely through the intermediate TPM⁺ formed by UV irradiation.

Such photoactivatable fluorescence was also found in some derivatives of TPOH. Compound 1-4 (Table S2, Supporting Information) all showed photoactivatable fluorescent properties both on surface and in aggregates similar to TPOH, despite of the dramatic difference in the fluorescence intensity (Figure S8 and S9). Compound 1 with Cl substituting the OH of TPOH, had strong fluorescence because of the good leaving group of Cl⁻. In contrast, MeO⁻ is a bad leaving group, so that compound 2 exhibited much weaker emission. The fluorescence of compound 3 was the weakest because of the quenching effect of three Cl substitutions on phenyl groups. Introducing an auxochrome MeO- onto one of the phenyl groups in compound 4 did not increase the fluorescence, probably because the UV light efficiently absorbed was not that efficiently used for photoactivation.

Inspired by the attractive fluorescence switches of TPOH between UV1 and UV2 irradiations reversibly on silica surface, we further applied it as rewritable photopatterning materials. As shown in Figure 4a, the blue fluorescent "CHEMISTRY" pattern was successfully printed on silica by 5 min UV1 irradiation under a photomask. The image was of high contrast because of the efficient "off-on" photoswitch. The photomask was then removed to "erase" the "CHEMISTRY" by UV1 irradiation for 5 min to light up the whole plate. After that, we covered the photomask again and irradiated the plate by UV2 for 30min. The dark "CHEMISTRY" in a bright background was generated. In addition, complicated patterns were also printed, erased and rewrote on this material with good resolution, such as an interesting "face changing" process. As illustrated in Figure 4b, two different Chinese paper-cut were used as photomasks. Upon sequential printing/erasing by UV1 and UV2, respectively, the two face images were switched between each other on a silica plate.

In summary, we investigated the photoactivatable AIE fluorescence of triphenylmethanol. The mechanism of this phenomenon is most likely through photo-induced generation of tritylium cation that is stabilized and fluorescent on solid surface or in aggregate states. The molecule was applied as a rewritable material for photopatterning solid-state fluorescence. By printing and erasing cycles through UV irradiation at 254 and 365 nm, the reversible photopatterning of "CHEMISTRY" and Chinese "face-changing" images was successfully achieved.

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