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Sensitive and Repeatable Photoinduced Luminescent Radicals from A Simple Organic Crystal

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Abstract: Photoinduced organic radicals are important for chemical and physical processes of organic materials, which are extensively investigated and applied in organic synthesis, photoelectronic devices, and biotechnology. However, there are rare reports of the luminescence for these photoinduced radicals, especially in the condensed state. Herein, an unexpected and interesting luminescent radical is described, which can be rapidly and reversibly generated from a simple organic crystal by gentle light irradiation in air. It was revealed that the twist and asymmetric conformation of isolated molecule in its crystal with only weak C-H⋯π intermolecular interactions, which led to the generation of such photoinduced luminescent radicals. In addition, dual-channel photosensitive device with rapid response and well repeatability can be obtained based on the thin film of this organic crystal, showing both photoswitching on luminescence and conducting.

Photoinduced radicals (PIR) materials have been widely studied and obtained brilliant applications in the fields of catalysis, polymerization, photoswitching and photodynamic therapy.[1] Extensive researches have been done on the photophysical properties of these highly reactive radicals in different states.[2] For example, there were many reports for photochromism of nitrogen-containing compounds, such as hexaarylbiimidazole derivatives in solution state,[3] and 2,4,6-tri(4-pyridyl)-1,3,5-triazine in crystalline state.[4] On the other hand, these photoinduced radicals are generally non-luminescent, in spite of their totally spin allowed radiative transition with doublet-spin excitons for high fluorescence.[5] This is because of the sufficiently stable of most isolated organic radicals under ambient conditions. Another important reason is that organic radicals suffered from aggregation-caused quenching of their luminescence in condensed state, by electron transfer or spin-exchange interaction.[6] As a result, there are few reports of photoinduced radicals with luminescence.[2a, 7] Recently, Tang *et al.* reported the phosphorus-containing compound, tris(4-chlorophenyl)phosphine, which can generate stable solid-state emissive radicals under UV irradiation.[8] Other examples were usually doped in polymer matrix with low concentration. Choi *et. al.* recently reported the white luminescence of phenothiazine-poly(dimethylsiloxane) hybrid system, which came from the integrated emissions of the molecules, radicals and cations of phenothiazine under air atmosphere.[9] But the radical species were generated slowly over hours by continuously irradiated with an UV lamp under air.

Triarylamine derivatives have been recognized as efficiently electroactive and photoactive materials, which readily produced radicals by electrochemical reaction/UV radiation and were intensively used in optoelectronic applications.[10] However, the luminescence of their photoinduced radicals have been rarely reported, especially in the condensed state.[11] Very surprisingly, obvious photoinduced luminescent radicals were unexpectedly observed from an organic crystal of substituted triphenylamine (tri-*p*-tolylamine, T3TA), when shone under UV light. This simple crystal exhibited interesting photoinduced luminescent color switching from blue to pinkish-purple, with a clear new emission peak at 580 nm, accompanied by the generation of triphenylamine radicals under light radiation in air. In addition, it is sensitive and repeatable of the generation and degradation of radicals to the UV radiation in the T3TA crystal. The radicals would immediately be created under light radiation, while they would degrade very fast after removal of the radiative light. Therefore, this T3TA crystal becomes a promising candidate for sensitive photoswitching with highly response speed based on luminescence on/off change. Moreover, high on/off gain of conductivity around 10^2 times can be obtained at a low applied voltage of 10 V, based on the photoconductive device fabricated by the T3TA polycrystalline thin film. These encouraging results provide new insights of the photoinduced radicals in condensed state as well as photosensitive materials with dual-channel switching for advanced optoelectronic devices applications.

When a polycrystalline solid of compound T3TA was continuously irradiated with an extra LED UV lamp (365 nm, lamp power: 5 W) at room temperature in air, the emission color of T3TA crystal would change from blue to pinkish-purple (Figure 1b and Video S1). At first glance, it looked like a photochromism for the T3TA crystal, which have been extensively reported for triarylamine derivatives before. When we checked the changes of its absorbance spectrum after light irradiation, there was no any

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obvious new peaks but only a red-shifted absorbance onset (~490 nm) in the spectrum (Figure S4). However, an obvious pinkish-purple light would appear when this experiment was carried out in dark. When observed in a fluorescence microscope, a clear red emission of the T3TA crystal can be seen from the red channel (580 nm, Figure S5). These results indicated that the color changes of the T3TA crystal under UV irradiation actually a photoinduced luminescence switching, which was unusual and further confirmed by the new emission peak arose at about 580 nm in its luminescent spectrum. As shown in Figure 1a, the intensity of this photoinduced luminescent peak significantly increased, as the irradiative time extended from 0.8 to 2.4 s. Additionally, this new peak cannot be detected after the T3TA crystal destroyed into amorphous powder, revealing the crystalline state an important assistance for this unusual phenomenon. Before continuously investigate such luminescence switching, the structure of T3TA crystal has been identified through analysis of nuclear magnetic resonance (NMR) and high-resolution mass spectrometer (HRMS) measurements (Figures S1-S3).

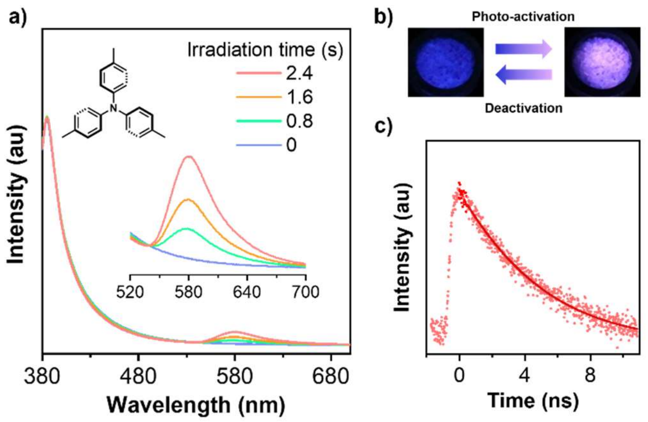

Figure 1. a) Photoluminescence spectra of T3TA crystal under UV light irradiation with different irradiation time: 0, 0.8, 1.6 and 2.4 s, respectively. The chemical structure of compound T3TA was inset; b) Photos of T3TA crystal taken under UV lamp irradiation without (left) and under (right) continuous irradiation; c) Luminescence intensity decay curve of T3TA crystal at 580 nm peak after it irradiated for 5 s.

Notably, this photoinduced new emissive peak is different from the phosphorescence peaks of T3TA crystal, which located at 490 and 520 nm at low temperature (Figure S6). The lifetime of this new peak at 580 nm was also measured and calculated as 4.2 ns, confirming its fluorescence characteristic (Figure 1c). So, we measured the electron paramagnetic resonance (EPR) spectrum of the irradiated T3TA crystal to check whether such new luminescence associated with the generation of radicals in T3TA crystal after irradiation. As shown in Figure 2a, prominent EPR signals with a *g* value[12] of 2.009 for radicals were observed in the irradiated crystal, displaying no hyperfine splitting. These EPR signals and the *g* value are similar to the reported ones[13] for radicals of triarylamine derivatives in solid state, which further confirmed the production of T3TA radicals in its crystal under light irradiation. In addition, the radicals were generated immediately when the T3TA crystal exposure to UV light. And these photoinduced radicals also disappeared rapidly after removing the irradiation light, as its EPR signals cannot be detected anymore. Furthermore, the intensity of luminescence and EPR of T3TA crystal would increase simultaneously when the UV irradiation intensity increased from 1% to 100%, as shown in the Figure S7. These results revealed that the unusual photoinduced color switching of T3TA crystal actually came from the photoinduced luminescent T3TA radicals in its crystal.

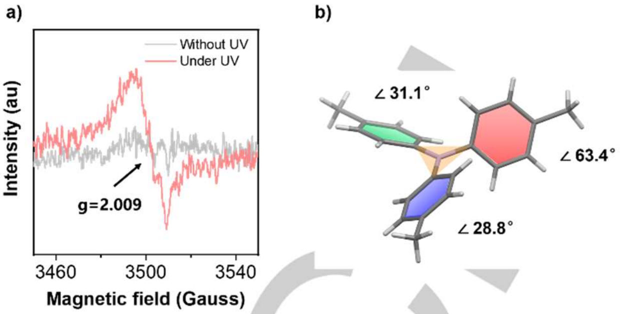

Figure 2. a) The electron paramagnetic resonance (EPR) spectra of T3TA crystal before and under UV light continuous irradiation; b) The conformation of T3TA in crystal, the angles between the three peripheral phenyl rings (red, green and purple ones) and the central tertiary amine plane (orange one) were inset.

In order to obtain insights of such sensitive photoinduced luminescent radical in crystalline state, the single-crystal of T3TA compound has been grown *via* solvent evaporation from its *n*-hexane solution. The X-ray diffraction (XRD) pattern of T3TA single-crystal was carefully analyzed, which revealed it a symmetry crystal with the space group C*i* of the triclinic system, as shown in Figure 2b. Notably, the central tertiary amine moiety exhibited a perfect plane (the light orange plane in Figure 2b), containing central N atom and the three C-N single bonds. This indicated the lone pair electrons of central N atom possessed good conjugation with these delocalized π electrons in the three peripheral phenyl rings. Similar to its analogues reported,[14] T3TA compound adopted a twist conformation in crystal, which peripheral phenyl rings kept certain directions out of the central tertiary amine plane. Besides, the dihedral angles between these phenyl rings and the amine plane are different. Especially, the angle of one phenyl ring (63.4°) was much bigger than those (28.8° and 31.1°) of the other two phenyl rings. As a result, the delocalized N lone pair electrons were partially limited in the central tertiary amine moiety and protected by these peripheral phenyl groups, which facilitated the generation of radicals under UV irradiation. Additionally, with such twist conformation, no any π-π stacking, neither face-to-face nor edge-to-edge packing, between T3TA molecules in the crystal can be found, as shown in Figures 3a-3c. On the other hand, the phenyl groups in T3TA molecule were restricted by lots of intermolecular C-H⋯π interactions. In Figure 3d, several weak C-H⋯π interactions were shown within distances of 3.082 to 3.368 Å, from the phenyl ring center to the hydrogen atom. Therefore, the photoinduced T3TA radicals were separated within one T3TA molecule, without transitions between T3TA molecules inside the crystal. The T3TA radical thus rapidly released its energy from its excited state to ground state *via.* light emission with peak at 580 nm of short lifetime (4.2 ns). Then the ground-state radicals continuous deformed back to neutral T3TA molecules.

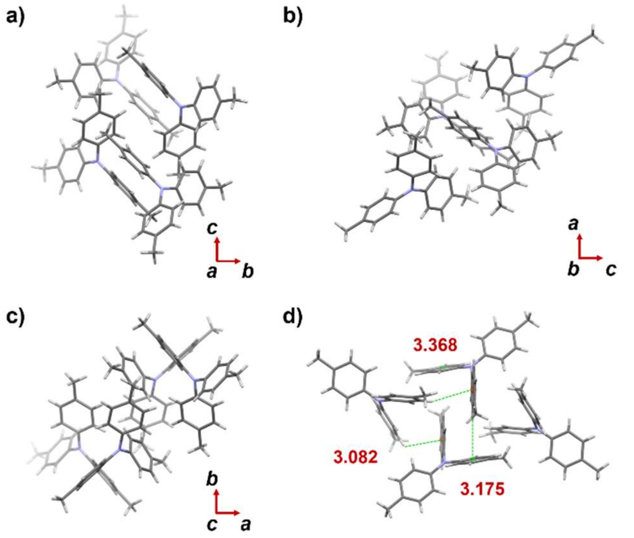

Figure 3. The molecular stacking and the intermolecular interactions inside T3TA single-crystal: a) view from *a*-axis; b) view from *b*-axis; c) view from *c*-axis; d) the weak C-H⋯π intermolecular interactions (green dashed line) and their distances. The distances (Å) of C-H⋯π interaction have been inset in d).

To further understand the radical generation mechanism of T3TA crystal, the nature of electronic states of T3TA molecules have been interpreted by density function theory (DFT) and time-dependent DFT (TD-DFT) calculations at the level of B3LYP/6-31G(d) based on the crystalline structure and an optimized conformation in gas state. The conformation of T3TA molecules were different in the two states, especially the structural symmetry. The T3TA molecule adopted an optimized conformation similar to C_{3V} symmetry in gas phase, with the similar angles between the phenyl moieties and the central amine plane (~41°, Figure 4a). Without typical donor-acceptor structure, the calculated results showed no obvious charge separation within the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in gas-phase state. However, one of the peripheral phenyl rings exhibited more twisted than the others in T3TA molecule in the crystalline state, which broke down the structural symmetry (the red phenyl ring in Figure 2b). This symmetry breaking actually resulted in a small charge separation within the HOMO and LUMO of T3TA molecule in crystalline state. As shown in Figure 4a, the electron cloud located on the more twisted phenyl ring (blue dashed circle) is slightly less than that on the other two phenyl rings within HOMO, while the contrary is the case within LUMO. It is reported that charge separation was in favor of the photo-induced radical generation. Thus the asymmetric conformation of T3TA molecule in crystalline state should promote radical generation under UV irradiation. The absorption and emission spectra of isolated T3TA molecule in crystalline state were also simulated by TD-DFT calculations based on its asymmetric structure, which were plotted in Figure 4b. The predicted spectra possessed absorption peak at ~290 nm and emission peak at ~380 nm, which exhibited good consistency with the experimental data (Figure 1a and S4).

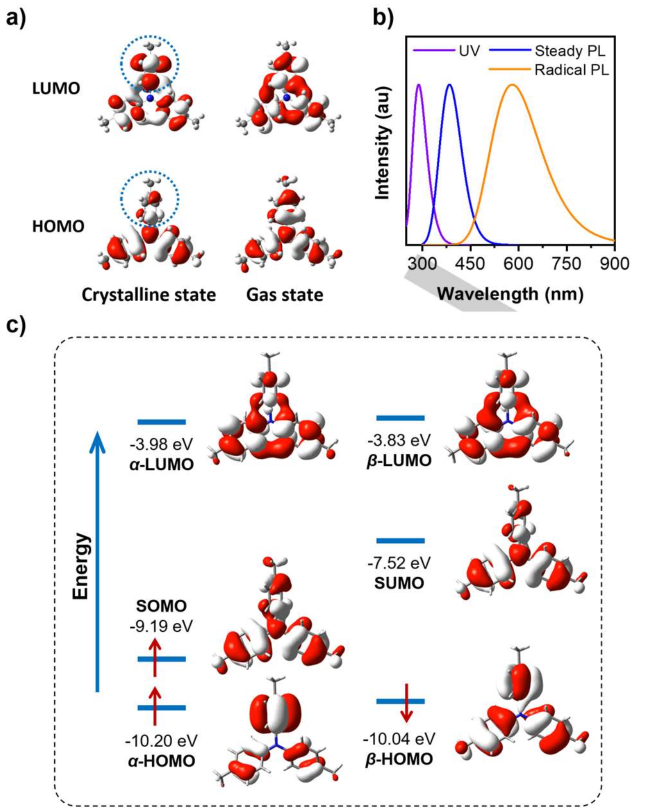

Figure 4. The emission spectra and electronic states of T3TA molecules interpreted by DFT calculations: a) molecular orbitals of T3TA molecule in crystalline and gas states at the level of B3LYP/6-31G(d); b) UV absorbance and photoluminescence spectra; c) the calculated energy level diagram and molecular orbitals of T3TA radical in crystalline state at the level of M06-2X/6-31G(d). The half-arrows indicate the state occupancy and electron spin orientation.

Additionally, an emission peak centered at around 580 nm for isolated T3TA cation could be found by the TD-DFT calculated results at the level of M06-2X/6-31G(d) in Figure 4b, which has an oscillator strength (*f*) of up to 0.1995 (*β*-HOMO → singly unoccupied molecular orbital (SUMO), ~2.52 eV, Figure 4c). Very interestingly, this peak located at the exact position of the photoinduced emission peak for the T3TA crystal in Figure 1a, which indicated such photo-induced luminescent species should be the T3TA radical cations. Furthermore, the detailed energy level diagrams and wave functions of the HOMOs and LUMOs of T3TA radical cation were in-depth analyzed (Figure 4c and S8). The electron cloud in MOs (HOMOs, LUMOs, SOMOs and SUMOs) spread over the whole T3TA molecule, without obvious separation. And the optimized conformation of T3TA radical cation in excited state also exhibited structural symmetry of C_{3V} similar to that of T3TA molecule in free state (Figure 4a). The three phenyl rings kept similar torsional angles of ~37° to the central amine plane, which are little smaller than those of free state T3TA molecule. As a result, T3TA radical cation would exhibit a conformation variation after excitation. As discussed above, there are no any obvious stacking but only weak intermolecular interactions between T3TA molecules in the crystal, such as weak C-H⋯π interactions. This conformational change thus became possible through phenyl rings rotations to a certain extent in the crystal by light irradiation. On the other hand, the excited-state T3TA radical cation also rapidly released its energy *via.* emission and came back to the original conformation in crystal, with those weak intermolecular C-H···π interactions inside the crystal. It matched well the short lifetime of new luminescence with peak at 580 nm in T3TA crystal. Therefore, the photoinduced luminescence switching of T3TA crystal originated from its radicals.

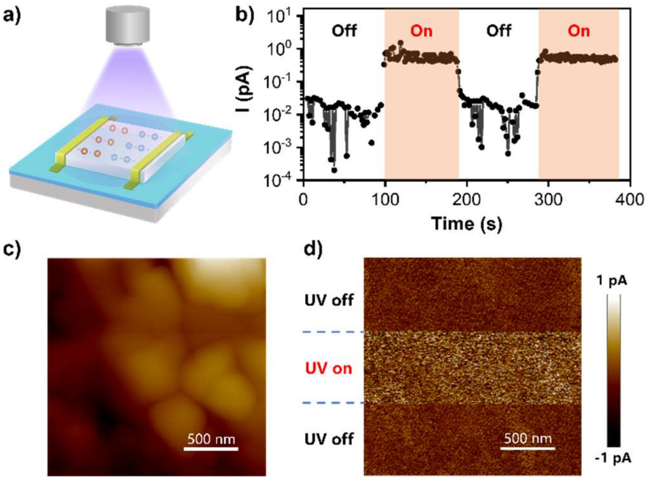

Figure 5. The photoconducting property of T3TA polycrystalline thin film by light irradiation: a) the schematic diagram of the photosensitive device based on T3TA crystal; b) the current switching of T3TA crystal along the light irradiation on and off; c) AFM and d) conductive AFM images of T3TA crystal along the UV irradiation on and off. The scale bars have been inset in c) and d).

This interesting photoinduced luminescence switching along radical generation in crystalline state make it suitable for dual-channel photosensitive device, as radical generation can also increase the material's conductivity. A simple photosensitive device with T3TA polycrystalline thin film was fabricated on glass with Au electrodes, as shown in Figure 5a. Upon UV light irradiation, the T3TA polycrystalline film showed not only luminescence switching (Figure 1b) but also clear photoconducting behavior (Figure 5b and S9-10), resulting in a dual-channel switching to irradiation in ambient conditions. As shown in Figure 5b, the conductivity jumped up and down along with the light irradiation switched on/off, with both a rapid responsibility and a well repeatability. The conductivity increased about 10^2 times at a low voltage of 10 V and a low light intensity of 10 mW cm^{-2}, suggesting photoexcitation of charge carrier in the crystal and sensitive photoresponse of the device. In addition, atomic force microscope (AFM) and conductive AFM images have been collected under a bias voltage of 2V (Figures 5c, 5d and S11), to further studied the changes on topography and surficial current of T3TA crystal with photoirradiation. The conductive AFM image showed a clear brighter contrast on the surface of T3TA crystal during the light irradiation, indicating an obvious current increase (Figure 5d). And this photocurrent rapidly and significantly switched as the UV light turned on and off, further conforming the sensitivity and repeatability of such photoconducting behavior. On the other hand, there were no changes on the topography of T3TA crystal, suggesting it a photoinduced electronic process as well. And the increasement of photoconductivity reduced along the UV light intensity decreased (Figure S12). It can be deduced that this changes on the conductivity was relative to the photoinduced radicals in T3TA crystal.

In conclusion, unexpected photoinduced luminescent radicals from an organic crystal of simple substituted triphenylamine compound (T3TA) has been carefully studied. Interestingly, the luminescent radicals can be generated in a rapid and repeatable way by exposed to gentle UV irradiation, which led to a dual-channel photoswitching of both luminescence and conducting. It was found that the T3TA molecules were separated in the crystal, with no any π-π stacking and only weak C-H···π interactions inside. And the twist and asymmetric conformation of the isolated T3TA molecule in this organic crystal facilitated the generations of radicals, based on the experimental and theoretical results. Therefore, photosensitive device with dual-channel photoswitching have been fabricated by T3TA polycrystalline thin film, showing both luminescence and conducting switching when triggered by UV light irradiation. It is notable that the photoconducting behavior was sensitive, with a high on/off gain around 10^2 times of photocurrent at a low voltage (10 V) and a low light intensity (10 mW cm^{-2}). Additionally, the dual-channel photoswitching can be well repeated with a rapid responsibility, as proved by the measurements of photoconducting and conductive AFM of the device. These results provide opportunity to design new optical and sensing systems for potential applications in light-operated switching and encryption based on photoinduced luminescent radicals. To explore more organic crystals with such interesting photoinduced response, lots of organic compounds will be tried in our lab in future.

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Keywords: photoinduced luminescence switching • radicals • photoconducting • organic crystal • rapid response

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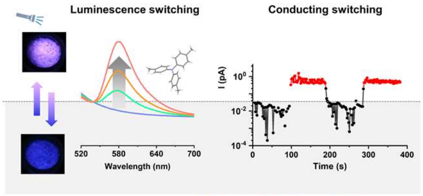

Sensitive and repeatable photoinduced luminescent radicals

Simultaneously dual-channel switching of luminescence and conducting can be achieved from a simple organic crystal by UV irradiation, which is because of the sensitive and repeatable generation of photoinduced luminescent radicals inside.