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#### Functional Structure/Activity Relationships

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# Exploration of highly efficient blue-violet light conversion agents for agricultural film based on structure optimization of TPA Yongtao Wang\*ab, Yongjiang Yu<sup>a</sup>, Wenjing Liu<sup>a</sup>, Litong Ren<sup>a</sup> and Guixian Ge\*a

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#### 8 Abstract

9 To obtain highly efficient blue-violet light conversion agents used for agricultural film, six 10 triarylacrylonitrile derivatives and their doping films were prepared. Further, the luminogens have 11 the ability to convert UV light into blue-violet light, and exhibit aggregation dependent fluorescence 12 emission and high-contrast fluorescence quantum yields from 0.004 to 0.833. Based on X-ray single 13 crystal diffraction analysis and aggregation-induced emission activity tests, the variant fluorescence 14 quantum yields are attributed to intermolecular  $\pi$ - $\pi$  stacking and phase transition between crystalline 15 state and amorphous state. In simulated greenhouse environment, the luminogens exhibit excellent 16 photostability. However, their fluorescence intensity drop to 17%-40% of prime intensity after 17 outdoor radiation for one month due to the ring-closing oxidation reaction (In summer). By 18 comprehensively considering the above photophysical properties and mechanical properties of the doping film, Ph4TPA is a potential light conversion agent for agricultural film in winter. More 19 20 importantly, the results indicate the properties of the light conversion films are expected to be further 21 improved by molecular design inhibiting the ring-closing oxidation reaction and dispersion of 22 crystalline nanoparticles in the doping film.

23 Keywords: Light conversion agents ; Light conversion film ; Acrylonitrile derivatives;
24 Photosynthesis; Fluorescence.

#### 25 **1. Introduction**

Light ecology studies have demonstrated the blue-violet light (400-480 nm) and red-orange light
 (600-700 nm) used as light fertilizer can enhance photosynthetic efficiency of crops<sup>1-3</sup>. The former

Electronic supplementary information (ESI) available: <sup>1</sup>H NMR, <sup>13</sup>C NMR, fluorescence, absorption, transmittance hydrogen bonding interaction and MALDI-TOF MS spectra. [Supplemental figures.]. See DOI: 10.1039/x0xx00000x

is beneficial to the increase of protein content, while the latter can promote synthesis of carbohydrate. 28 29 Further, the light conversion shed film experiments show that growth cycle of crops, insect pests 30 and ultraviolet damage to polymer matrix are obviously reduced or shortened, meanwhile, quality 31 and yields of crops are significantly increased<sup>4-9</sup>. Therefore, the light conversion agents used for 32 agricultural film have received extensive attention and great progress have been made in the past 33 decades. However, the light conversion agents still face some problems such as spectra matching, 34 fluorescence quantum yield (PLQY) and weather resistance. How to design highly efficient light 35 conversion agents has become a very tricky thing.

36 To achieve perfect match with the absorption spectra of chlorophyll a, b and carotenoid in the blue-37 violet region, the light conversion agents with short conjugate structure or weak intramolecular charge transfer (ICT) should be adopted to realize a wide energy band gap<sup>10-11</sup>. As a matter of fact, 38 39 the shortage and lag of efficient deep-blue organic light-emitting materials indicate molecular design 40 of blue-violet light conversion agents will be full of frustrations for a given period of time. In 41 addition, aggregation caused quenching is another culprit restricting the effect of light conversion. 42 Fortunately, aggregation-induced emission luminogens (AIE) with twisted or propeller-like 43 molecular configuration are induced to emit efficiently in the aggregated state, but non-emissive in the dissolved form<sup>12-15</sup>. In our previous research work, tetraphenylethylene (TPE) derivatives with 44 45 AIE activity, twisted diaryl ketones with thermal delayed fluorescent performance and 46 triphenylacrylonitrile (TPA) were chosen as light conversion materials. The results indicated that 47 TPE derivatives easily suffered from photo-oxidation leading to faint emission, while diaryl ketones 48 were ruled out because of weak fluorescence and their depressing mechanical properties. 49 Interestingly, TPA doped polyvinyl chloride (PVC) films exhibited deep-blue fluorescence emission and excellent mechanical properties<sup>16</sup>. In comparison with TPE derivatives, TPA exhibits better 50 51 photostability due to electron-withdrawing effect of cyanide inducing reduction of the electron cloud density of benzene ring<sup>17-19</sup>. Even so, TPA still cannot meet the request of practical application 52 53 because of low PLQY and unsatisfactory photostability.

To obtain highly efficient blue-violet light conversion agents and reveal the key factors affecting
the light conversion performance, in this paper, five novel triarylacrylonitrile derivatives named as
PhMe3TPA, PhMeO3TPA, Ph3TPA, Ph4TPA and PhMe4TPA were designed and synthesized (As

57 shown in Scheme 1). The significantly enhanced PLQYs have been realized for crystal Ph4TPA and 58 PhMe3TPA compared with that of TPA. Based on X-ray single crystal diffraction analysis, the 59 marked difference of PLQY between Ph3TPA and PhMe3TPA are mainly attributed to different 60 molecular packing and arrangement. Unfortunately, the triarylacrylonitrile derivatives exhibit 61 inferior PLQY in PVC doped films. To make clear the latent mechanism of remarkable PLQY 62 reduction in PVC doped films, AIE activity test and the morphology regulation of nanoparticles are 63 completed by mixing THF/H<sub>2</sub>O and adding the cetyltrimethylammonium bromide (CTAB), 64 obviously, crystallization-induced emission enhancement (CIEE) active characteristics and 65 aggregation dependent fluorescence cause the deterioration of PLQY in PVC doped films. Further, 66 the inherent mechanism of photodegradation are analyzed and discussed by changing temperature, 67 light intensity, aggregation state and molecular structure. The results show the crystalline state is not only conducive to maintaining high PLQY, but also improving the photostability of the light 68 69 conversion materials.

70 2. Experimental details

#### 71 **2.1 Measurements and characterizations**

72 The UV-vis spectra were determined on a Mapada UV-3200pcs spectrophotometer. Fluorescence 73 measurements were taken on Agilent Cary Eclipse fluorescence spectrophotometer. <sup>1</sup>H NMR and 74 <sup>13</sup>C NMR spectra were obtained with a Varian inova instrument at 400 MHz and 100 MHz using tetramethylsiane (TMS) as the internal standard, and CDCl3 as the solvent in all cases. 75 76 MALDI/FIRMS were recorded on an Ultrafle Xtreme MALDI-TOF/TOF mass spectrometer 77 (Bruker, Germany). Fluorescence microscopy photos were obtained on OLYMPUS BX53. 78 Photodegradation experiments were carried out by a 300W xenon lamp equipped with a filter, and 79 radiation intensity of artificial sunlight is up to 129 Mw/cm<sup>2</sup>.

80 **2.2 Materials and synthesis** 

THF, DMF and toluene were dried according to standardized procedures previously described. All the other chemicals and reagents used in this study were of analytical grade without further purification. In general, all the intermediates and final compounds were purified by column chromatography of silica gel (200-300 mesh), and the reaction process was monitored by thin-layer

chromatography (TLC). The synthetic methods of intermediates and target compounds were shown
as Scheme 1. The synthetic method of TPA was carried out according to the reported literature<sup>17</sup>.
The light conversion films were prepared by referring to our previous method<sup>20</sup>, obtaining final

films with a 1% mass fraction.



89 90

Scheme 1. Synthetic routes of the luminogens.

91 2-(3-bromophenyl)-3, 3-diphenylacrylonitrile (1): In a three-necked round-bottom flask (250 mL) 92 equipped with a reflux condenser were placed benzophenone (4.00 g, 22 mmol), NaH (60%, 1 g, 25 93 mmol) and anhydrous toluene (50 mL) under nitrogen. The mixture was refluxed for 10 min. Then, 94 3-bromophenylacetonitrile (3.88 g, 20 mmol) in toluene (60 mL) was added dropwise over 1 h under 95 reflux condition. Evolved H<sub>2</sub> was observed at the oil bubbler and the reaction was lasted for another 96 20 h. Upon cooling to room temperature, 100 mL of water was added to the mixture. The organic 97 layer was collected and washed with brine three times. Next, the organic phase was dried over 98 anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. Then, the crude product was purified by column 99 chromatography to give white solid. Yield: 83%.

2-(4-bromophenyl)-3,3-diphenylacrylonitrile(2): The compound was synthesized by the same
 procedure described for compound 1 using 4-bromophenylacetonitrile and benzophenone, the crude
 product was purified by chromatography (silica gel, DCM: petroleum=1:10). White solid was
 obtained. Yield: 76%.

104 2-(2'-methyl-[1,1'-biphenyl]-3-yl)-3,3-diphenylacrylonitrile(PhMe3TPA): Into a three-necked 105 round-bottom flask (100 mL) equipped with a reflux condenser were placed compound 1 (1.80 g, 5 106 mmol), o-tolylboronic acid (0.82 g, 6 mmol), CH<sub>3</sub>COOK (1.17 g, 12 mmol), a mixed solution (toluene: H<sub>2</sub>O=5:1, 20 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.17 g, 0.15 mmol) under argon atmosphere. And then, 107 108 the mixture was refluxed for 12 h under argon. After cooling to room temperature, the reaction 109 mixture was poured into water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuum. The crude product was purified by 110 111 chromatography (silica gel, ethyl acetate: petroleum=1:6). White solid was obtained. Yield: 81%. m.p. 115.3-117.0 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.50-7.39 (m, J = 4.9 Hz, 7H), 7.38-112 113 7.26 (m, 2H), 7.26-7.10 (m, 6H), 7.08-7.01 (m, 2H), 6.92 (d, J = 7.3 Hz, 1H), 1.98 (d, J = 1.4 Hz, 114 3H). (Fig. S6). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.06, 142.22, 140.93, 140.36, 139.20, 135.23, 134.79, 130.93, 130.88, 130.20, 129.93, 129.63, 129.20, 128.95, 128.48, 128.44, 128.38, 127.95, 115 116 127.46, 125.69, 120.14, 111.58, 20.20. (Fig. S7). HRMS (MALDI-TOF): m/z 371.1660, calculated 371.1674. (Fig. S8). 117

2-([1,1'-biphenyl]-3-yl)-3,3-diphenylacrylonitrile(Ph3TPA): The compound was synthesized by 118 119 the same procedure described for PhMe3TPA using compound 1 (1.80 g, 5 mmol), phenylboronic 120 acid (0.732 g, 6 mmol), the crude product was purified by chromatography (silica gel, DCM: petroleum=1:10). White solid was obtained. Yield: 81%. m.p. 135.8-137.0 °C. <sup>1</sup>H NMR (400 121 122 MHz, Chloroform-d) & 7.53-7.42 (m, 7H), 7.39-7.33 (m, 2H), 7.33-7.25 (m, 7H), 7.24-7.21 (m, 1H), 7.12-7.04 (m, 2H). (Fig. S9). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.18, 141.47, 140.47, 140.38, 139.39, 123 124 135.27, 130.92, 130.08, 130.06, 129.16, 129.07, 128.86, 128.83, 128.62, 128.54, 128.53, 127.65, 127.24, 127.16, 120.20, 111.68. (Fig. S10). HRMS (MALDI-TOF): m/z 357.1506, calculated 125 126 357.1517. (Fig. S11).

**2-(4'-methoxy-[1,1'-biphenyl]-3-yl)-3,3-diphenylacrylonitrile(PhMeO3TPA):** The compound was synthesized by the same procedure described for PhMe3TPA using compound **1** and (4methoxyphenyl)boronic acid, the crude product was purified by chromatography (silica gel, DCM: petroleum=1:10). White solid was obtained. Yield: 89%. m.p. 145.2-147.0 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.50-7.37 (m, 7H), 7.33-7.25 (m, 3H), 7.25-7.19 (m, 4H), 7.07 (dt, *J* = 8.5, 1.9 Hz, 2H), 6.92-6.86 (m, 2H), 3.82 (s, 3H). (Fig. S12). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.32, 157.93,

- 133 140.92, 140.39, 139.32, 135.06, 132.78, 130.80, 129.94, 129.92, 128.99, 128.89, 128.48, 128.38,
- 134 128.27, 128.07, 127.82, 126.68, 120.10, 114.15, 111.67, 55.35. (Fig. S13). HRMS (MALDI-TOF):
- 135 m/z 387.1661, calculated 387.1623. (Fig. S14).

136 2-(2'-methyl-[1,1'-biphenyl]-4-yl)-3,3-diphenylacrylonitrile(PhMe4TPA): The compound was 137 synthesized by the same procedure described for PhMe3TPA using compound 2 and o-tolylboronic 138 acid, the crude product was purified by chromatography (silica gel, DCM: petroleum=1:10). White solid was obtained. Yield: 79%. m.p. 162.8-164.0 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-139 140 *d*) δ 7.49 (dt, *J* = 6.5, 1.9 Hz, 2H), 7.47-7.40 (m, 3H), 7.30 (ddt, *J* = 12.7, 9.2, 2.9 Hz, 4H), 7.26-7.16 (m, 7H), 7.07 (dt, J = 8.5, 1.9 Hz, 2H), 2.24 (s, 3H). (Fig. S15). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 141 142 8 158.14, 142.46, 141.38, 140.88, 139.59, 135.68, 133.73, 131.27, 130.87, 130.40, 130.34, 130.03, 143 129.87, 129.73, 129.49, 128.92, 128.69, 127.98, 126.27, 120.62, 111.84, 20.84. (Fig. S16). HRMS (MALDI-TOF): m/z 371.1668, calculated 371.1674. (Fig. S17). 144 2-([1,1'-biphenyl]-4-yl)-3,3-diphenylacrylonitrile(Ph4TPA): The compound was synthesized by 145 the same procedure described for PhMe3TPA using compound 2 and phenylboronic acid, the crude 146

147 product was purified by chromatography (silica gel, DCM: petroleum=1:10). White solid was

148 obtained. Yield: 59%. m.p. 136.3-137.2 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.58-7.53 (m,

149 2H), 7.49-7.38 (m, 9H), 7.36-7.31 (m, 3H), 7.29-7.25 (m, 1H), 7.24-7.18 (m, 2H), 7.08-7.04 (m,

150 2H). (Fig. S18). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.65, 140.98, 140.49, 140.03, 139.17, 133.74,

151 130.80, 130.14, 129.98, 129.91, 129.07, 128.48, 128.36, 127.71, 127.03, 126.98, 120.13, 111.29,

152 77.36, 77.04, 76.73. (Fig. S19). HRMS (MALDI-TOF): m/z 357.1513, calculated 357.1517.

153 (Fig. S20).

3-mesityl-2-phenylacrylonitrile (tMePCN): The compound was synthesized by the same method described for MePCN. Yield: 89%. m.p. 96.8-98.5 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.847.57 (m, 3H), 7.53 -7.39 (m, 3H), 6.95 (s, 2H), 2.31 (s, 9H). (Fig. S21). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)
δ 142.73, 138.35, 135.81, 133.17, 130.60, 129.19, 128.90, 128.51, 125.71, 118.46, 116.69, 20.94,

158 20.09. (Fig. S22). HRMS (MALDI-TOF) m/z: Mass 247.1361, Calc. Mass 247.1361. (Fig. S23).

159 10-phenylphenanthrene-9-carbonitrile (PPACN) m.p. 183.2-185.0 °C. <sup>1</sup>H NMR (400 MHz,

160 Chloroform-d)  $\delta 8.81-8.73$  (m, 2H), 8.44-8.36 (m, 1H), 7.84-7.75 (m, 3H), 7.71 (d, J = 8.3 Hz, 1H),

161 7.65-7.55 (m, 4H), 7.54-7.47 (m, 2H) (Fig. S24). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.40, 137.03,

- 162 131.77, 130.18, 129.92, 129.62, 129.44, 128.93, 128.84, 128.73, 128.66, 128.33, 128.07, 127.41,
- 163 126.48, 122.90, 117.26, 109.62 (Fig. S25). HRMS (MALDI-TOF) m/z: Mass 279.1048, Calc. Mass
- 164 279.3420. (Fig. S26).

#### 165 **3. Results and discussion**

#### **3.1 Photophysical properties of triarylacrylonitrile derivatives**



**Fig. 1.** The UV-visible absorption and fluorescence spectra of the luminogens. (a) UV-vis spectra in THF  $(1x10^{-5} \text{ mol/L})$  (b) fluorescence spectra in THF  $(1x10^{-5} \text{ mol/L})$  (c) fluorescence spectra in crystalline state (d) fluorescence spectra in PVC film.

To investigate photophysical properties of the dyes, the corresponding THF solutions  $(1 \times 10^{-5} \text{ mol})$ 170 171 L<sup>-1</sup>) and PVC doped films were prepared. As shown in Fig. 1, PhMeO3TPA showed different UVvis spectra compared to the other four compounds. PhMe3TPA, Ph3TPA, Ph4TPA and PhMe4TPA 172 have two obvious absorption bands located at 230-280nm and 280-400nm respectively, while 173 174 PhMeO3TPA shows four absorption bands without clear boundary. The differences should be 175 attributed to the stronger electron donating ability of -OCH<sub>3</sub>, which induces ICT effect and produces new absorption bands. Compared with meta-substitution, para-substitution is beneficial to extension 176 of conjugate structure. Accordingly, the maximum absorption peaks of Ph4TPA and PhMe4TPA 177

show obvious red-shifted than that of the other three dyes, and so do emission maxima. Contrary to 178 179 electron donating ability, the maximum emission peaks of PhMeO3TPA, PhMe3TPA and Ph3TPA 180 exhibit bathochromic shift in turn, and the twisted conformation induced by Me- and MeO- groups 181 is suggested to be a possible reason of abnormal shifts further discussed in the part of the crystal 182 analysis. Compared with THF solution, the emission maxima of luminogens show red shift of 40-70nm at solid state and in PVC doped films, especially marked red shifts for solid state due to 183 molecular stacking and arrangement. In addition, PhMe4TPA exhibits two splitting emission peaks 184 185 in PVC doped films, indicating different electronic structures between PhMe4TPA and the other luminogens. Based on UV absorption and blue-violet light emission spectra of the luminogens, they 186 187 are suitable sunlight conversion agents used for agricultural film.

188 Generally, the transmission curve is used to investigate the conversion efficiency of UV, 189 transmittance of visible light and the proper addition ratio of light conversion agents in polymer 190 matrix. As shown in Figure S1, the UV-vis transmittance curve of the PVC doped films indicate the 191 transmittance between 200nm and 400nm reduces significantly, which means most of ultraviolet 192 irradiation are absorbed and converted. Meanwhile, the visible light (400-700 nm) transmittance of 193 the doped films remains a tiny change, even a slight increase for PhMe3TPA, Ph3TPA and Ph4TPA, 194 which indicates the transmittance of visible light is not affected by doping of the luminogens. 195 According to the reported literature<sup>20</sup>, transmittance of light conversion films and PVC blank film 196 are calculated at 200-390nm and 400-700nm respectively. As shown in Fig 2, less than 7.5% UV 197 transmittance for all the doping films means 1% weight ratio of light conversion agents relative to 198 PVC is appropriate.

199 The decrease in UV transmittance means that UV is converted into desired blue-violet light, but it 200 may also be thermal radiation. Thus, the integral area of emission spectra should be the more proper 201 evaluation indicator than transmittance for the light conversion properties of the luminogens. 202 Considering absorption maxima of chlorophyll a (430 nm) and b (450 nm), integral area of blue-203 violet light should be confined to 400-480nm. Under the excitation wavelength of 317 nm and 351 204 nm, Ph4TPA exhibits the largest the integral area among of the dyes via direct visual observation, 205 and excitation dependent fluorescence emission due to molecular tumbling (Fig. 3). Obviously, 206 choosing Ph4TPA as sunlight conversion agent should be the wisest decision purely from the light

#### 207 conversion efficiency of view.





Fig. 2 Transmittance of the doping films at 200-390 nm and 400-700 nm.

#### **3.2 Fluorescence quantum efficiency and x-ray single-crystal analysis**



Fig. 3 The fluorescence spectra of the luminogens in PVC films under excitation at 317 nm(a) and 351 nm(b).

- 210 The luminogens with minor structural differences show high-contrast fluorescence emission. Based
- on naked eye observation, the fluorescence of PhMe3TPA and TPA is faint compared to that of the



others in THF solution, while PhMe3TPA, PhMe4TPA, Ph4TPA and TPA exhibit strong
fluorescence emission in crystalline state (Fig. 4). Obviously, PhMeO3TPA and Ph3TPA belong to
traditional fluorophores with the aggregation-caused quenching (ACQ) effect, while PhMe3TPA,
PhMe4TPA, Ph4TPA and TPA, especially for PhMe3TPA and Ph4TPA have excellent CIEE
characteristic. Further, the absolute PLQYs of the luminogens are obtained in crystalline state and
PVC film by adopting integrating sphere method, and the relative PLQYs in different solvents are
calculated by using quinine sulphate as a standard, which testify the above results (Fig. 4).

Fig. 4 PLQYs and pictures of the luminogens under UV-irradiation (a) in THF solution (1x10<sup>-</sup>

<sup>5</sup>mol/L) (b) in crystalline state (c) in PVC film (fluorescence microscopy photos).

221 However, the CIEE-active luminogens suffer from serious decreasing PLOY in doping film 222 compared with crystalline state. To make clear the internal mechanism, firstly, crystal culture and 223 analysis of Ph3TPA (CCDC 1870773) and PhMe3TPA (CCDC 1870774) with opposite characteristic are completed. Secondly, AIE activity of PhMeO3TPA, Ph4TPA and PhMe4TPA are 224 225 tested in THF-water mixture. Thirdly, fluorescence changes of Ph4TPA are observed by adding CTAB in mixed solution of THF/H<sub>2</sub>O. The crystal Ph3TPA was a triclinic system with the space 226 group P - I (a = 8.9129(9) Å, b = 10.4465(12) Å, c = 11.1785(11) Å;  $\alpha = 107.535(7)^{\circ}$ ,  $\beta = 93.797(7)^{\circ}$ , 227 228  $\gamma = 98.838(7)^{\circ}$ ). Two adjacent molecules with tail-to-tail arrangement linked together by two intermolecular C-N...H hydrogen bonds (d = 2.722 Å) and terrible  $\pi$ - $\pi$  stacking (d = 3.566 Å), and 229

230 the strong intermolecular hydrogen bond and  $\pi$ - $\pi$  stacking make molecules to form a dimer (Fig. 5), 231 leading to red-shifted and weak fluorescence emission. The crystal PhMe3TPA is a monoclinic 232 system with the space group P 21/c (a = 13.874(6) Å, b = 10.834(5) Å, c = 16.943(6) Å;  $\alpha = 90^{\circ}$ ,  $\beta$ =  $123.73(2)^\circ$ ,  $\gamma = 90^\circ$ ). Intermolecular hydrogen bonds play a major role in the molecular packing 233 and every one molecule is connected with adjacent six molecules by C-N...H (CH<sub>3</sub>), C-H...C and 234 235 N-C...C interactions, forming three-dimensional space structure, however, no  $\pi$ - $\pi$  stacking was 236 observed due to steric effect of methyl leading to significantly increased the dihedral angle between 237 A ring and B ring (Fig. S2 and Fig. 5). Obviously, two compounds possess twisted molecular 238 configuration, but different hydrogen bonds, molecular arrangement and intermolecular  $\pi$ - $\pi$ 239 stacking, triggering two different fluorescence emission. For typical AIE luminogens, the 240 fluorescence emission intensity is gradually increase with the addition of poor solvent. Figure S3 indicates that PhMeO3TPA, Ph4TPA and PhMe4TPA present different characteristics in THF and 241 242 THF/water mixtures with varying water fractions. Compared with THF solution, the fluorescence 243 intensity of PhMeO3TPA remains an obvious increase in the  $H_2O/THF$  mixtures from 10% to 40%, 244 then drops fast. Similar to PhMeO3TPA, Ph4TPA also shows decreasing fluorescence after the first 245 increase. Different from PhMeO3TPA and Ph4TPA, continuous fluorescence reduction appeared 246 for PhMe4TPA. The complex fluorescence phenomenon should be attributed to solvent polarity and 247 formation of aggregation state. When the ratio of  $H_2O/THF$  increases, the increased solvent polarity 248 is beneficial to stabilize the ground state and excited state of polar molecules, thereby reducing non 249 radiation and enhancing fluorescence emission. If the increased ratio leads to unordered and loose 250 nanoparticles, the following fluorescence quenching will occur. In addition, the maximum fluorescence emission wavelength of three luminogens red shift continuously with the increase of 251 252 solvent polarity, which hinted the luminogens have ICT characteristic. Finally, the amorphous film 253 of PhMe3TPA was prepared by spin casting its dichloromethane (DCM) solution on a glass sheet 254 and rapidly drying under vacuum, and showed very weak emission under UV light. Based on the 255 above results, the inferior PLQY of doping film should be attributed to the aggregation dependent emission, by the preparation and doping of crystalline nanoparticles, PLQY of PhMe3TPA and 256 Ph4TPA doping film should be sharply improved. Peng et al regulate the packing and arrangement 257 of molecules by surfactants and obtain self-assembled polymorphs<sup>21</sup>, based on this idea, CTAB is 258

- 259 selected to optimize the fluorescence emission of TPA in aggregated state. Then, enhanced
- 260 fluorescence emission was observed, but its effect is not significant (Fig. S4).

#### 261 **3.3 Photothermal stability**



**Fig. 5** Single crystal structure and molecular stacking mode of crystal Ph3TPA (a) and crystal PhMe3TPA (b).

262 Under sunlight irradiation, free radicals are easily generated and lead to degradation of luminogens. 263 In addition, temperature is another important factor triggering photodegradation of organic dyes. 264 Combining aggregation dependent PLQYs of the luminogens, four variables including light 265 intensity, temperature, crystalline state and amorphous state were investigated to explore the critical 266 factor of photothermal stability. Silver-foiled crystal and amorphous TPA were putted into an oven 267 at 50 °C, 60 °C and 70 °C for a night, but no new dot was found by thin layer chromatography, 268 illustrating TPA was stable and insensitive to temperature. Then, crystal (slow solvent evaporation) 269 and amorphous (rapid evaporation of CH<sub>2</sub>Cl<sub>2</sub> solution on quartz sheet) TPA were irradiated under 270 8 W ultraviolet lamp at 365 nm for 24 h, and the radiation process did not cause an obvious increase 271 in temperature. As a result, there was still no new product to be detected. Next, crystal and 272 amorphous TPA was placed in a quartz bottle and radiated under sunlight for one month (in summer). Crystal TPA exhibited excellent stability, but a new product was found in amorphous sample. 273 274 Further, the oxidation product induced by ring-closing reaction was separated, purified and 275 characterized by HR-MS and NMR. Thereby, it is inferred that amorphous state and strong light 276 radiation can accelerate the ring-closing reaction of TPA. In the crystalline state, weak bond 277 interactions and ordered arrangement are not destroyed, which is helpful to inhibit rotation of

278 benzene rings and the resulting oxidation reaction. Besides, the strong light radiation usually results 279 in a rise in temperature, thereby activation of the rotation and vibration of bonds, and thus TPA is 280 instable under sunlight, but remains stable under the low power ultraviolet lamp. Fortunately, the 281 suitable temperature of crops growth is between 20 °C and 30°C. At this suitable temperature, the 282 luminogens show excellent stability after 100 minutes of irradiation (Fig. 6). However, the intensity 283 of fluorescence emission changed dramatically when the doping films were placed outdoor for 30 days in summer (Fig. S5), which may be due to ACQ characteristic of oxidation products induced 284 285 (Fig. S27). As a conclusion, Ph3TPA and PhMe3TPA are potential light conversion agents for agricultural film in winter due to below 30°C inside the greenhouse. To inhibit the fore-mentioned 286 287 oxidation reaction, tMePCN are synthesized by simple condensation reaction of aryl aldehyde and 288 aryl acetonitrile. Because of occupation of active site by 2, 6-dimethy of tMePCN, photostability of luminogens is expected to be improved. Luckily, occupation of active site should be an effective 289 290 method inhibiting the ring-closing oxidation reaction, and the new substances is not found in 291 tMePCN sample under strengthening solar radiation (129 mW/cm<sup>2</sup>).





PhMeO3TPA(e) in PVC films under artificial sunlight irradiation at different times.

#### 294 **3.4 Mechanical properties**

Referring to our previously reported methods, the mechanical properties of doping films and PVC
blank film were studied (Table 1). By contrast, PhMe4TPA exhibits the worst elongation among

these doping films, more interesting, elongation of Ph3TPA and Ph4TPA is better than that of PhMe3TPA and PhMe4TPA respectively. Obviously, methyl substituent is detrimental to elongation, and the reason may be methyl substituent causes twisted molecular configuration, thereby reduces intermolecular interactions. Different from elongation, tensile stress of all the doping films are improved to some degree compared with that of PVC blank film.

302 Table 1 Mechanical property of light conversion films

Fata -	Elongation (%)	Tensile stress(MPa)	Thickness
Entry -	Transverse/Portrait	Transverse/Portrait	(mm)
PhMeO3TPA	10.01/12.40	37.60/33.77	0.051
PhMe3TPA	15.68/20.01	37.63/48.50	0.042
Ph3TPA	18.56/34.75	35.60/49.67	0.038
Ph4TPA	13.28/25.41	39.38/47.98	0.039
PhMe4TPA	4.25/4.90	44.57/33.58	0.040
PVC	13.50/12.49	33.13/31.20	0.053

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In summary, we designed and synthesized six triarylacrylonitrile and one diarylacrylonitrile 304 305 derivatives to obtain highly efficient blue-violet light conversion agents for agricultural film. 306 Despite similar molecular structures, serious  $\pi$ - $\pi$  stacking furnished PhMeO3TPA and Ph3TPA with ACQ characteristic, while PhMe3TPA, PhMe4TPA, Ph4TPA and TPA exhibited CIEE 307 308 characteristic, showing strong fluorescence in the crystalline state. More importantly, the 309 luminogens exhibited aggregation dependent fluorescence leading to undesirable PLQY in doping film. Even so, PLOY of Ph4TPA is up to 0.833 and 0.107 in solid state and doping film respectively, 310 which are almost 4 times and 5 times that of TPA in corresponding state. Furthermore, the 311 312 fluorescence emission intensity of the doping films displays slight changes for 100 min under a 313 simulated greenhouse environment, however, only 15%-40% of the original intensity was retained due to the increase of light intensity after outdoor exposure to sunlight in summer for one month. 314 Photothermal stability test further indicated crystalline state can improve potostability of dyes 315 compared with amorphous state, and the ring-closing oxidation reaction is the main cause of the 316 decrease of fluorescence intensity, but the reaction can be effectively inhibited by occupying active 317 318 site. Last but not least, Ph4TPA has potential application value as blue-violet light conversion agent

- in winter, and preparation of crystalline nanoparticles and dispersion of Ph4TPA in polymer matrix
- will be very important to further improve the efficiency of light conversion and photostability, while
- 321 occupation of active site will offer theoretical guidance and practical reference for next step
- 322 molecular design of light conversion agents for agricultural film.
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### 407 Exploration of highly efficient blue-violet light conversion agents for

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# agricultural film based on structure optimization of TPA

- 409 High contrast PLQYS of luminogens with tiny structural differences in solution,
- 410 crystalline and doping films

a PhMeO3TF	PA PhMe3TPA	РһЗТРА	Ph4TPA	PhMe4TPA	ТРА
Φ <sub>f</sub> =36%	Φ <sub>1</sub> =3%	Φ <sub>f</sub> =15%	Φ <sub>f</sub> =28%	Φ <sub>f</sub> =24%	Φ <sub>f</sub> =14%
b Ф <sub>r</sub> =0.4%	Φ <sub>r</sub> =57.6%	Φ <sub>r</sub> =0.5%	Φ <sub>r</sub> =83.3%	<b>Φ</b> <sub>r</sub> =30.8%	<b>φ</b> <sub>r</sub> =22.4%
С					

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