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Exploring the high efficient light conversion agents for agricultural film based on aggregation induced emission effects

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Yunpeng Qi, Yongtao Wang,* Yongjiang Yu, Zhiyong Liu, Yan Zhang, Yu Qi and Changtong Zhou

Abstract: Aggregation-induced emission (AIE) is a unique photo-physical phenomenon and has become an emerging and hot research area. It has a wide range of applications for its excellent luminous. In this paper, five compounds and their corresponding light conversion films were prepared based on AIE effects and thermally activated delayed fluorescence (TADF) phenomenon. Further, ultraviolet conversion, dispersion and photo-physical property such as UV-vis spectra, fluorescence spectra, photo stability as well as mechanical property of light conversion films were investigated in detail. The results reveal that triphenylacrylonitrile (TPA) exhibits excellent photo stability and ultraviolet light conversion property. In addition, the fluorescent emission spectrum of TPA corresponds well with the absorption spectrum of the plants at blue-violet region. Especially, light conversion film added TPA also shows enhanced mechanical property and slightly lower visible light transmittance (3.79%) than PVC blank film. Based on photo stability of five compounds, it can be concluded that the electron-withdrawing cyano group can increase photo stability of TPA, while carbazole substituents are proved to be uncertain to the rate of photo oxidation, which is attributed to electron-donating property of carbazole and increased molecular distortion or rigidity. Finally, it is worth mentioning that utilizing AIE-active luminogens (AIEgens) in agricultural light conversion film field is first time.

Introduction

As the old saying goes, “All life on our earth depends on the sun ". Through plant photosynthesis, crops can convert carbon dioxide and water into human foods. However, not all sunlight are beneficial to plant photosynthesis, among them, the blue-violet light (400-480 nm) and red-orange light (600-700 nm) are beneficial to plant growth and development, while the yellow-green light (510-580 nm) are almost reflected completely by plants leaves, the ultraviolet (280-380 nm) light not only can increase plant diseases and insect pests, but also lead to oxidative degradation of agricultural polyethylene film. To make full use of solar energy, it is an important and challenging task for the light conversion agents by converting ultraviolet and yellow-green light into blue-violet and red-orange light respectively. Experiments of the light conversion film for crops on farmland show that: the light conversion agricultural films can shorten the growth cycle of crops, increase yield of crops, and improve quality of crops[1-4]. However, the existing light conversion agents have such drawbacks as single light conversion, poor stability, unsuitable fluorescence matching with crops absorption spectrum. Thus, research and exploitation of the novel high-efficient light conversion agents are also urgent.

Fortunately, an interesting phenomenon, aggregation induced emission (AIE) effect, was discovered by *Tang et al* research team in 2001[5, 6], the AIE luminogens does not emit light or emit faint light in solution, however, the compounds emit strong fluorescence at aggregate state or solid state. Beyond all question, taking full advantage of the solid-state fluorescence emission enhancement characteristics, AIE luminogens are expected to be excellent light conversion agents used in agricultural film. Currently, AIE-active luminogens have become a hot research topic for their potential application in various fields, such as light emitting diodes[7-11], light-harvesting[12], optical storage[13-18], optical memories[19-21], mechanical sensors[22, 23], chemosensing and bioimaging[24-29]. Besides, AIE materials systems have been developed such as hexaphenylsilole[5], pyran derivatives[30-34], 9,10-disubstituted anthracene derivatives[35-38], difluoroboron avobenzone[39-45], tetraphenylpyrazine[46, 47], tetraphenylethene (TPE)[48-58], triphenylacrylonitrile (TPA)[59-61]. Among of them, TPE and TPA are the most famous AIE luminogens and building block for the construction of AIE fluorophores because of propeller-shaped non-planar molecule conformation, facile synthesis and excellent AIE effect. Therefore, in this paper, five AIE-active compounds and a synthetic intermediate, named successively TPE, TPA, DTBE-TPE, TTBC-TPE and DTBC-DPK, were synthesized. Furthermore, a series of tests including the light stability in solution and polyvinyl chloride (PVC) film,

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School of Chemistry and Chemical Engineering/Engineering Research Center of Materials-oriented Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, P. R. China. E-mail: wyt_shzu@163.com; Fax: +86 993 2057270; Tel: +86 993 2057277

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ultraviolet conversion, dispersion state in PVC film as well as corresponding mechanical properties were studied. As far as our knowledge, this is the first report of AIE-active light conversion agents for the purpose of agricultural application.

Results and discussion

Photophysical Properties

The UV-vis absorption spectra of TPE, TPA, DTBC-DPK, TTBC-TPE and DTBC-TPE in dilute THF solution (1×10^{-5} mol/L) and PVC films (addition of 1% by weight of AIE luminogens to PVC) are investigated, as shown in Fig. 1. DTBC-TPE, TTBC-TPE and DTBC-DBK emerge three absorption bands, TPE and TPA give two absorption bands at ultraviolet region in THF solvent. Different from the UV-vis absorption in THF solvent, the ultraviolet absorption region of the luminogens in PVC films are expanded. Meanwhile, the blank PVC film showed little absorption. Consequently, we can tentatively draw the following conclusions, the increase of ultraviolet absorption region are not directly origin from PVC films, but due to the change of peripheral environment of the AIE luminogens. On the other hand, It also preliminary indicates that these AIE luminogens are suitable as light conversion agents owe to the excellent ability to absorb ultraviolet light.

In order to further understand the Light conversion behaviour of the AIE luminogen, take an example, the excitation spectrum of TPA in PVC film and solid state are tested. As shown in the Fig. 2, the excitation intensity scopes almost cover the whole ultraviolet region and exhibit two main excitation bands at wavelength of 280 nm and 360 nm, which is almost no distinction compared to solid state, this may be due to the fact that TPA retains similar morphology in solid state and PVC film.

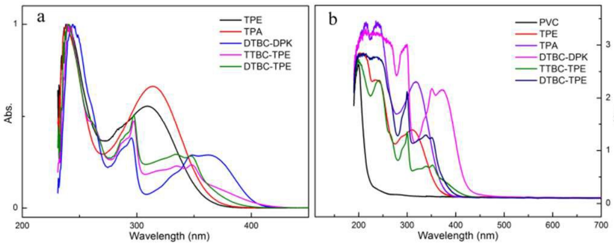

Fig. 1 UV-vis absorption spectra of five compounds in THF (a) and PVC film (b).

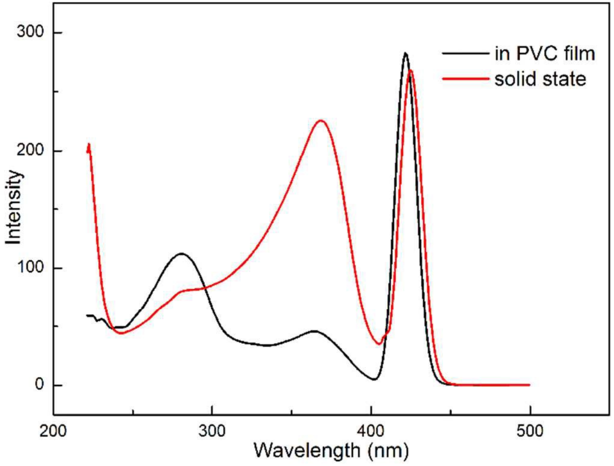

Fig. 2 The excitation spectrum of TPA in PVC film and solid state (emission wavelength: 420 nm).

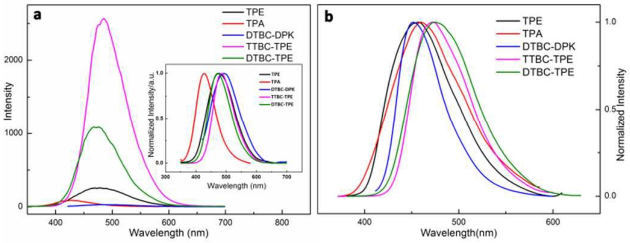

Fig. 3 Fluorescence spectra of TPE, TPA, DTBC-DPK, TTBC-TPE and DTBC-TPE in PVC films (a) and solid state (b). Inset: normalized fluorescence spectra of them in PVC films (1% mass fraction).

TPE, TPA, DTBC-DPK, TTBC-TPE and DTBC-TPE are all exhibit AIE-activity, however, their fluorescence emission properties are quite different. As shown in the Fig. 3, TTBC-TPE and DTBC-TPE give strong emission intensity at maximum wavelength of 483 nm and 462 nm in PVC film, respectively. The fluorescence emission peak of TPE and TPA located at 478 nm and 430 nm, respectively, while the fluorescence intensity was declined compared with TTBC-TPE and DTBC-TPE, the possible reason is that the decreasing molecular conjugation is not beneficial to electron transfer and transition. More seriously, there is almost no fluorescence is observed for DTBC-DPK. Combining with the intense fluorescence emission of DTBC-DPK in solid crystalline state or aggregate state, we have reason to suspect that DTBC-DPK is hold the amorphous state in PVC film, the amorphous state leads to relatively weak intermolecular force, increasing intramolecular rotations and stretching vibration, which cause the energy relaxation via non-radiative channel, subsequently, the above sharp fluorescence quench happened. Therefore, it is obvious that PVC matrix can affect the fluorescence intensity of luminogens, but whether different impacts are also exist in the emission wavelength? By compared with fluorescence emission spectra in solid state, the emission peak of TPE, DTBC-DPK and TTBC-TPE showed a red shift of 23 nm, 40 nm and 11 nm in the PVC film, respectively. By contrast, TPA and DTBC-TPE show a blue shift of 31 nm and 13 nm in PVC film, respectively. The shift of fluorescence emission peak is usually related to the different molecular packing or crystalline morphologies. However, the packing or morphology is difficult to be predicted. Further, the shifts of the emission wavelength of the corresponding PVC films are investigated by thermal treatment. As a result, there are almost no change in their emission wavelength after heated two hours at 120℃ for these PVC films except DTBC-DPK is observed to be blue shifted (～16 nm). It is probably due

Table 1. Fluorescence emission wavelength of five compounds at different state.

	Wavelength (nm)			Width of half peak (nm)	
Entry	In PVC film	Ss[a]	As[b]	In PVC film	Ss[a]
TPE	478	455	465	115	83
TPA	430	461	400	62	88
DTBC-DPK	492	452	485	102	55
TTBC-TPE	483	472	508	71	70
DTBC-TPE	462	475	497	81	80

[a] Ss:Solid state of compounds; [b] As: Aggregation state of compounds.

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to the DTBC-DPK keep a thermodynamic metastable state in PVC film. In addition, the width of half peak (FWHF) is also an important parameter. Generally, the bigger is FWHF, the less uniform is crystal particles. As shown in Table 1, the FWHF is increased after dispersed the light conversion agents in PVC films for TPE and DTBC-DPK, no obvious change for TTBC-TPE and DTBC-TPE, and decreased for TPA, which further indicate that TTBC-TPE, DTBC-TPE and TPA also maintain excellent crystal state, while TPE and DTBC-DPK transformed to amorphous state from crystal state in PVC films. Based on the data from UV-vis absorption spectra, excitation spectra and fluorescence spectra, TPE, TPA, DTBC-DPK, TTBC-TPE and DTBC-TPE could efficiently convert the ultraviolet light into blue light in both solution and PVC films, and their fluorescence emission spectra could match with blue light region of plant photosynthesis. Compared with TPE and DTBC-DPK, TPA, DTBC-TPE and TTBC-TPE are the better light conversion materials using for agriculture film.

In order to evaluate the photo stability of five luminogens, the fluorescence spectra of them in PVC films are recorded under artificial sunlight irradiation at different times. As shown in Fig. S1 and Fig. S3, the fluorescence emission peak of TPE films has no obvious changes after exposed to photo irradiation two hours, after radiated three hours, the fluorescence intensity began to decrease rapidly and a novel peak emerged at about 400 nm, the fluorescence intensity of peak located at about 470 nm is reduced to half of its original and the novel peak increased obviously when radiated time reach to four hours. DTBC-DPK film exhibit strong sensitivity to light irradiation, after twenty minutes, the luminescence peak of DTBC-DPK film appeared blue shift, and the fluorescence intensity declined radically. TTBC-TPE films show similar fluorescence emitting behaviour to DTBC-TPE films because of their molecular structure are analogous, the fluorescence intensity of DTBC-TPE decayed when radiated for two hours with artificial sunlight, but fluorescence of TTBC-TPE film receded until radiated time reach to three hours. It indicates that TTBC-TPE film is more stable than DTBC-TPE film which probably due to the bigger periphery substitutions of TPE in TTBC-TPE, which is more effective to inhibit rotation of molecular bonds. The above four light convention films all suffered some degree of fluorescence decay in artificial sunlight condition, however, TPA film display excellent photo stability even if in long irradiation time which was reach to four hours. Then, the fluorescence spectra of them in aggregated state are also investigated in detail, the solid nano-particle of five compounds could suspended evenly in THF/water mixture. As shown in Fig. S2 and Fig.S4, the fluorescence spectra of TPE, DTBC-DPK, TTBC-TPE and DTBC-TPE all shows time-dependent degradation trend, and degradation rate is faster than in PVC films. Fluorescence intensity of TPE and DTBC-TPE reduced by around eighty percent and seventy percent, respectively, after radiated with artificial sunlight for an hour and a half. For TTBC-TPE and DTBC-TPE, their fluorescence intensity began to reduce obviously after radiated for twenty minutes and almost depleted when radiated time reach to an hour and a half. Pleasantly, TPA still exhibit remarkable photo stability. But an abnormal phenomenon occurred in its fluorescence spectra, where the fluorescence intensity did not decrease but enhance after photo irradiation. To explain this abnormal phenomenon, the same experiments are repeated, but the same result is obtained. According to some related literature home and abroad, some AIE-active compounds show morphology-dependent fluorescence, thus, we inferred that the abnormal phenomenon results from the change of aggregation morphology of suspended particle in the THF/water mixture. In the course of the above experiments, some particle visible to the naked eye have formed which did not exist in as-prepared mixture. To further confirm that, the particle size of as-prepared mixture and photo radiated mixture are tested by zeta/nano particle analyzer. As shown in Fig. 4, the particle size distribution of TPA in as–prepared mixture was mainly range from 100 nm to 1000nm, and calculated particle average size is 427 nm, four types of different size of particle formed in photo irradiated mixture, the calculated average size are 10 nm, 176 nm, 1348 nm and 29992 nm, respectively. Indeed, the particle size of the as-prepared mixture has changed after photo irradiation, which indicated that particle size of TPA could affect the fluorescence intensity. In addition, to further investigate the anti-photo degradation ability of them, we have carried out oxidation reaction of them with 2,3-dichloro-5,6-dicyano-1,4- benzoquinone(DDQ). The results show that all of them could be oxidized by DDQ to varying degrees (oxidation products of TTBC-TPE, DTBC-TPE and DTBC-DPK can be detected by TLC, and the yields of TTBC-TPE and DTBC-TPE are very low) except TPA. *Zhu et al*[62] had reported previously that TPE could be oxidized and generated DPP. Hence, it is a better way to estimate and judge the stability of TPA by the

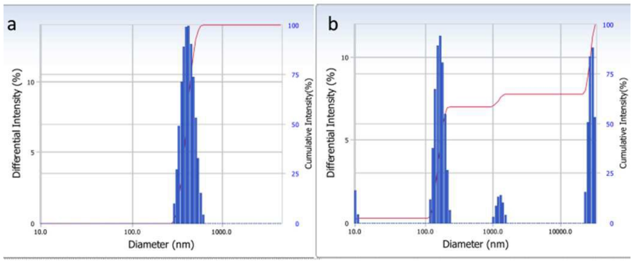

Fig. 4 The particle distribution of TPA in as-prepared mixture (a) and after photo irradiation (b).

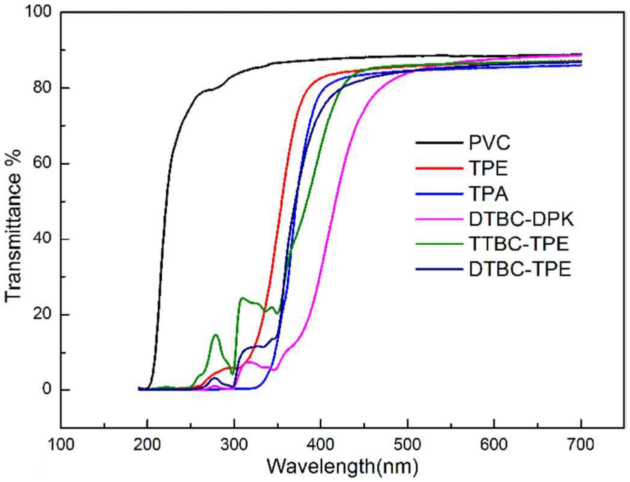

Fig. 5 UV-visible transmittance spectra of TPE, TPA, DTBC-DPK, TTBC-TPE, DTBC-TPE in PVC films and blank PVC film.

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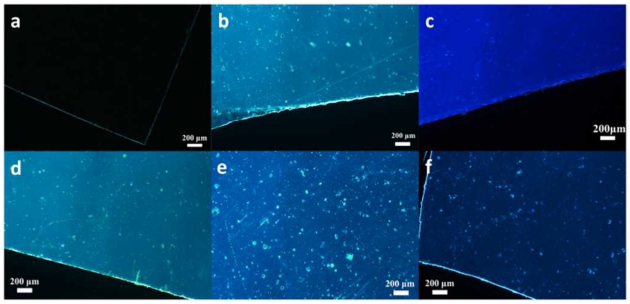

Fig. 6 Fluorescence microscopy photos of blank PVC (a), and TPE (b), TPA (c), DTBC-DPK(d), TTBC-TPE (e), DTBC-TPE (f) in PVC films under UV-irradiation.

electron density of benzene rings. As electron withdrawing group, acrylonitrile unit of TPA was able to reduce electronic cloud of benzene rings, which caused TPA could not degrade whether treated by photo irradiation or chemical reaction.

UV-visible transmittance analysis of light conversion films

Transmittance is one of the important properties of light convention films, in addition, it is known that the doping of light conversion agent could affect the transmittance to some extent, so it is necessary to observe and study the transmittance spectra of light conversion films. As shown in Fig. 5, detail data are calculated by integrated area of transmittance curve and summarized in Table 2. The ultraviolet (200nm-380nm) transmittance are vary from TPE to DTBC-TPE, among them, TPA give a very low transmittance in ultraviolet region which is as lower as 6.83%, the transmittance of other four light conversion films in ultraviolet region are higher than TPA film except DTBC-DPK. Whereas, ultraviolet light almost entirely penetrated through the blank PVC film. It suggest that ultraviolet light could be shielded effectively by these light conversion agents. The visible light (400nm-700nm) transmittance of these light conversion films are hold ca. 85%, and reduced compare to the blank PVC film but only have a tiny change, which indicated that the doping of light conversion agents only faintly affect the visible light transmittance of PVC film. The excellent transmittance of these light conversion film are ascribe to the good compatibility and dispersibility of luminogens which will mentioned below.

Table 2. Light transmittance of light conversion films.

Entry	UV light (200nm-380nm)	Visible light (400nm-700nm)
PVC	72.90%	88.44%
TPE	15.98%	85.97%
TPA	6.83%	84.65
DTBC-DPK	3.58%	80.95%
TTBC-TPE	13.81%	85.10%
DTBC-TPE	10.09%	84.53%

Table 3. Mechanical property of light conversion films.

Entry	Tensile stress (Mpa)	Elongation (%)	Thickness(mm)
	Transverse/Portrait	Transverse/Portrait	
PVC	24.63/25.55	19.26/15.62	0.054
TPE	41.03/40.07	11.72/47.68	0.034
TPA	45.08/45.58	41.09/67.17	0.062
DTBC-DPK	33.03/32.54	03.77/05.01	0.076
TTBC-TPE	30.41/28.39	04.96/18.50	0.032
DTBC-TPE	38.86/33.55	17.54/11.02	0.034

Compatibility and dispersibility of light conversion films

We utilized fluorescence microscopy to evaluate the compatibility and dispersibility of luminogens in light conversion films, the fluorescence microscopy photos shown in Fig. 6. The blank PVC film has no fluorescence, only give a dark image, other five light conversion films show obvious blue fluorescence in different extent. In addition, we could find that some bright unformed particles homogeneously dispersed in PVC films. The fluorescence images illustrated that these light conversion films possess good dispersibility and compatibility.

Mechanical property

We referred the national standards of People's Republic of China (GB/13022-91) employed the mechanical strength testing of light conversion films. The stretching speed is setted as 2mm/min. The thickness of light conversion films are tested by millesima thickness gauge/AICE. All data are summarized in Table 3. The thickness data is average value which calculated by five random test point of light conversion film. From the data we known that the tensile stress of dispersed light conversion agents films are increased compared to the blank PVC film, especially, TPA film increased near 2 folds. The elongation also have changed to some extent after doped the light conversion agents in the PVC film, DTBC-DPK film suffered significantly impact which indicated it is very brittle, elongation of TTBC-DPK film and DTBC-TPE film are also decreased. But, elongation of TPE film and TPA film are increased intensively, indicated they have excellent elasticity.

Experimental

Measurement and characterization.

^{1}H NMR spectra and ^{13}C NMR spectra were obtained with a Varian inova instrument at 400 MHz and 100 MHz using tetramethylsilane (TMS) as the internal standard, and $CDCl_3$ as the solvent in all cases. The UV-vis absorption spectra were obtained on a MaPada UV-3200PCS spectrophotometer. Fluorescent emission spectra were obtained on a Hitachi F-2500 fluorescence spectrophotometer. MALDI/HRMS was record on an UltrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker, Germany). Digital photographs were taken by Canon 550D (Canon, Japan) digital cameras. Fluorescence microscopy photos were obtained on OLYMPUS BX53.

Materials.

THF and CH_2Cl_2 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 on silica gel (200-300 mesh), and crystallization from analytical grade solvents. Reactions were monitored by using thin layer chromatography (TLC).

Synthesis.

The molecules structure for TPE, TPA, DTBC-TPE, TTBC-TPE and DTBC-DPK are shown in Scheme 1. TPE and TPA were synthesized according to the McMurry coupling reaction; for DTBC-TPE, TTBC-TPE and DTBC-PM, t-butyl-carbazole (TBC) was introduced at first, then, McMurry coupling reaction occurred with Benzophenone, to thus give final molecules; The target molecules were characterized by ^{1}H NMR, ^{13}C NMR, MALDITOF mass spectrometry.

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Preparation of 2,3,3-triphenylacrylonitrile (TPA)

In a dual-neck flask diphenyl ketone (5.8 g, 22.3 mmol) and sodium cyanide (1.1 g, 60%) are dissolved into 30 mL anhydrous toluene, stirred 30min at 90 ℃ under argon atmosphere, then benzene acetonitrile (4.7 g, 23.5 mmol) in 20 mL anhydrous toluene solution was slowly added drop wise in 1 h. The reaction mixture was reacted for 10 h at 90℃. Upon cooling, the mixture was poured into 100 mL ice water, and washed by saturated sodium chloride solution three times. Then, extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was purified by chromatography (silica gel, CH_2Cl_2/petroleum ether). Yellowish solid was obtained. Yield: 42%; ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 7.45-7.42 (m, 5H) 7.26-7.17 (m, 8H), 7.01-6.99 (m, 2H) (Fig. S8); ^{13}C NMR (100 MHz, CDCl3): δ/ppm = 157.79, 140.44, 139.08, 130.81, 129.95, 129.90, 129.74, 129.02, 128.52, 128.49, 128.39, 128.27(Fig. S9). HRMS (MALDI-TOF): m/z 282.0 calculated 281.1 (Fig. S16).

Preparation of 1,1,2,2-tetraphenylethene (TPE)

In an oven-dried dual-necked flask equipped with a stir-magneton, diphenyl ketone (1.44g, 8.0mmol) and zinc powder (2.08g, 32mmol) were combined. A balloon filled with argon was connected to the dual-necked flask via the side tube and purged for 3 times，Then dried THF (50mL) was added to the tube via a double needle at vacuum condition, and move on to a cryostat stir 10 min at -78 ℃. At last, titanium tetrachloride (1.73ml, 16mmol) was added via syringe, stir 30min sequentially, after that move out them from the cryostat and cool down to room temperature naturally. The dual-necked was heated at 80 ℃ for 24 hours and then cooled to room temperature. The reaction was quenched by water and added K_2CO_3 (10%) solution. Then, extracted with $CHCl_3$ three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained. Yield 70%, after purification by flash chromatography on silica gel with petroleum ether/ethyl acetate, v/v =20/1.

Preparation of (9,10-diphenylphenanthrene) (DPP).

A 0.1 M solution of tetraphenylethylene (TPE) in a 1:9 mixture of methanesulfonic acid and dichloromethane (10 mL) was reacted with 1 equiv of 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) at ~0 ℃, under an argon atmosphere, to afford a blue-violet solution[63] which turned brown during the course of 30 min. The resulting brown mixture was quenched by added saturated aqueous sodium bicarbonate solution (20 mL). The dichloromethane layer was separated and washed with a saturated brine solution (2×10 mL), dried over anhydrous Na_2SO_4, and evaporated to afford the corresponding DPP in quantitative yield.^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 8.85 (d,J=8.4, 2H), 7.72-7.68 (m, 2H), 7.59 (dd,J1=4.0, J2=8.0, 2H), 7.54-7.50 (m, 2H), 7.27-7.18 (m, 10H) (Fig. S10).

Preparation of 9,9'-((2,2-diphenylethene-1,1-diyl)bis(4,1-phenylene)) bis(3,6-di-tert-butyl-9H-carbazole) (DTBC-TPE).

The compound was synthesized by the same procedure described for TPE using bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)methanone and diphenyl ketone. The crude product was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether). Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 8.14 (d,J=1.6 4H), 7.48 (dd,J1=2.0,J2=8.4, 4H), 7.39-7.34 (m, 12H), 7.24-7.16 (m, 10H), 1.49 (s, 36H) (Fig. S11); ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 143.53, 142.96, 142.56, 142.15, 139.65, 139.26, 136.62, 132.81, 131.57, 127.98, 127.01, 126.02, 123.70, 123.50, 116.34, 109.41, 34.89, 32.18 (Fig. S12). HRMS (MALDI-TOF): m/z 886.5201, calculated 886.5221 (Fig. S18).

Preparation of 1,1,2,2-tetrakis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)ethane (TTBC-TPE).

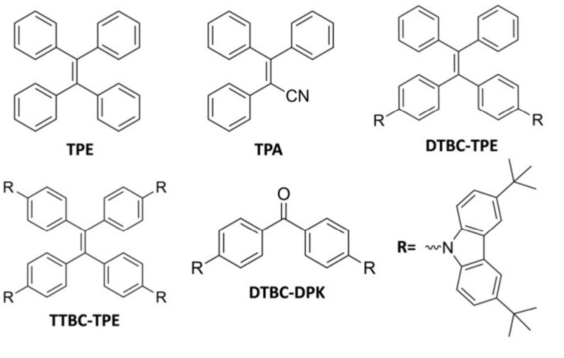
This compound was prepared by following the synthetic procedure described for TPE using bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)methanone. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether). Yield: 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 8.14 (s, 8H), 7.52-7.47 (m, 16H), 7.40 (d,J=0.8, 16H), 1.45 (s, 72H) (Fig. S13); ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm =142.98， 141.65， 139.05，137.00， 132.82， 125.98, 123.69， 123.49, 116.27， 109.28， 34.76， 32.06 (Fig. S14).

Preparation of bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)methanone (DTBC-DPK).

In a dual-neck flask 3,6-di-tert-butyl-9H-carbazole (TBC) (5.58 g, 20 mmol) and potassium tert-butoxide (3.37 g 30 mmol) are dissolved into 30 mL anhydrous DMF, then bis(4-fluorophenyl) methanone (2.18 g, 10 mmol) in 30 mL anhydrous DMF solution was slowly added drop wise in 1 h under a argon atmosphere. The reaction mixture was reacted for 10 h at 110 ℃. Upon cooling, the mixture was poured into 200 mL ice water, then a deep yellow solid precipitate was filtered off and washed with ethanol. After vacuum drying the crude product and purified by chromatography (silica gel, CH_2Cl_2/petroleum ether). 5.16 g of yellow solid was obtained. Yield: 70%. ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 8.15 (d,J=8.0, 8H), 7.78 (d,J=8.0, 4H), 7.50 (d,J=1.2, 8H), 1.48 (s, 36H) (Fig. S15); HRMS (MALDI-TOF): m/z 736.3, calculated 736.4 (Fig. S17).

Preparation of light conversion films.

In an oven-dried flask equipped with a mechanical stirrer polyvinyl chloride (PVC) (4.95g) and TPA (0.05g) were dissolved into 30 mL THF. The mixture was stirred for 12 h at room temperature. After that, placed the flask into a ultrasonic oscillators for 30 min to remove the bubbles of the mixture. Then the mixture was poured onto a prepared glass plate and paved rapidly with a glass rod. Finally, put them into ventilated cabinets until the THF was volatilized completely, obtained a contents of TPA was 1% (mass fraction) light conversion film of TPA. The light conversion films of TPE, DTBC-TPE, TTBC-TPE, DTBC-DBK was prepared by the same procedure describe for TPA, obtain final films of them with 1% mass fraction.



Scheme 1. Molecular structure of light conversion agents.

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Photodegradation of compounds in PVC films and aggregate state. Photodegradation experiments was carried out by a 300W xenon lamp equipped with a filter which providing artificial sunlight about 10 cm away from the aqueous solution and sample of PVC films containing all compounds. The aqueous suspensions containing all necessary compounds (in the THF–H_2O mixtures, where compounds could easily dissolve in THF, and water was used because it is a non-solvent, the molecules must aggregate in the aqueous mixtures) were put in a custom quartz container which could not absorbed light irradiation.

Conclusions

In summary, we have explored a new type of light conversion film based on AIEgens, obtain a potential light conversion agent via screen several typical AIEgens. Light conversion film of TPA not only could effectively convert ultraviolet light (200nm-380nm) into blue light (the maximum emission wavelength was 430nm), but also possess excellent photo and chemical stability. Their mechanical property and transmittance were investigated in detail, result show that the addition of AIEgens could not decreased the mechanical property of PVC film except DTBC-DPK film, and the visible light (400nm-700nm) transmittance of these light conversion films are hold ca. 85%. In addition, these light conversion films possess good dispersibility and compatibility. This work furnishes a promising platform for the agricultural light conversion area, and has advantage of cost compare to traditional rare metal contained light conversion films.

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