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A tetraphenylethene-based caged compound: synthesis, properties and applications†

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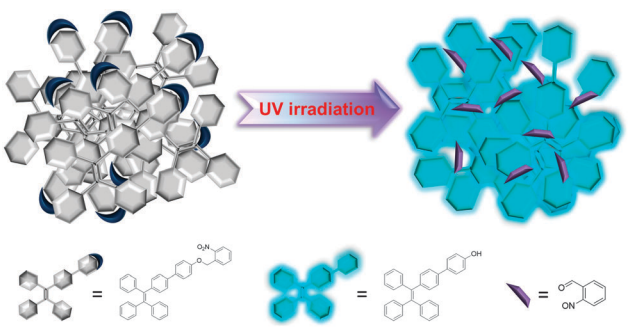
Chris Y. Y. Yu,[a] Ryan T. K. Kwok,[a] Ju Mei,[a] Yuning Hong,[a] Sijie Chen,[a] Jacky W. Y. Lam[a] and Ben Zhong Tang*[abc]

A tetraphenylethene-based caged compound (TPE-C) is designed and synthesized. TPE-C is non-fluorescent either in solution or in aggregated state, but its emission can be induced to emit strong cyan emission in the aggregated state by UV irradiation. This property enables TPE-C to be applied in photo-patterning and anti-counterfeiting related areas.

The development of fluorescent materials with high solid-state quantum yield is of practical importance because most of their real-world applications require the use of materials in aggregated state or even in solid state.[1,2] Fluorophores with aggregation-induced emission (AIE) characteristics have emerged as a novel class of materials which could meet such requirements due to their good photostability, high photo-bleaching resistance and high quantum yields in aggregated state.[3] So far, a variety of functional materials based on AIE fluorophores have been extensively reported and a number of stimuli responsive systems have been constructed with AIE materials.[3,4] A photo-activatable AIE system, however, is still rare.

Caged fluorophores, whose emission is partially or completely quenched by a quencher but can be recovered upon cleavage of the quencher under certain stimuli, such as UV or thermal treatment, are a type of typical photoactivatable materials and have been well studied and applied in many technological fields especially those related to biological applications such as macromolecular movement tracking and super-resolution imaging.[5–9] A 2-nitrobenzyl group is the most representative quencher for caged fluorophores.[5–9] Because of the strong electron-withdrawing ability of the 2-nitrobenzyl group, the emission of fluorophores in the caged compound is quenched through the photo-induced electron transfer (PeT) process. Once the 2-nitrobenzyl group is cleaved by UV irradiation, the emission of the fluorophore will be recovered. Conventional fluorophores such as BODIPY, fluorescein, and rhodamine have been widely used in the caged systems.[6–9] Their emissions can be recovered almost completely after UV treatment in solution. However, the recovery efficiency is not satisfactory in the aggregated state. Only weak or no emission can be observed even after a long time of UV irradiation because the emission of uncaged fluorophores is quenched by aggregation-caused quenching (ACQ). Hence such an ACQ effect greatly limits the applications of the caged compounds in the aggregated state.

Herein, we reported a new caged compound (TPE-C), which was constructed by using an AIE-active tetraphenylethene (TPE) derivative as a fluorophore with a 2-nitrobenzene group as a quencher. TPE-C is non-fluorescent either in solution or in aggregated state but its emission in the aggregated state can be photoactivated upon UV irradiation and consequently a strong cyan emission is observed (Scheme 1). The fluorescence response to the UV-irradiation endows the TPE-C with the potential to be applied in photo-patterning and anti-counterfeiting related areas.



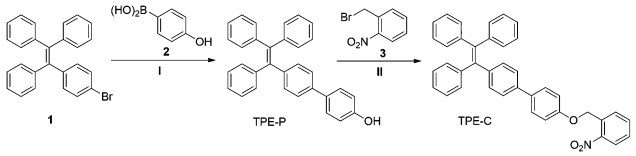
Scheme 1 Uncaging process of TPE-C.

[a] *Department of Chemistry, HKUST Jockey Club Institute for Advanced Study, Division of Biomedical Engineering, Division of Life Science, State Key Laboratory of Molecular Neuroscience and Institute of Molecular Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk*

[b] *Guangdong Innovative Research Team, SCUT-HKUST joint Research Laboratory, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

[c] *HKUST Shenzhen Research Institute, No. 9 Yuexing First RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China*

† Electronic supplementary information (ESI) available: Detailed synthesis and characterization of TPE-P and TPE-C; UV and PL spectra of TPE-C; photographs of TPE-C under UV irradiation; HPLC of TPE-C with different irradiation times and photo-patterning and pattern erasing. See DOI: 10.1039/c4cc03337j



Scheme 2 Synthetic route to TPE-P and TPE-C. (I) $Pd(PPh_3)_4$, Na_2CO_3, THF–H_2O, reflux overnight; (II) Cs_2CO_3, MeCN, 80 °C, 8 h.

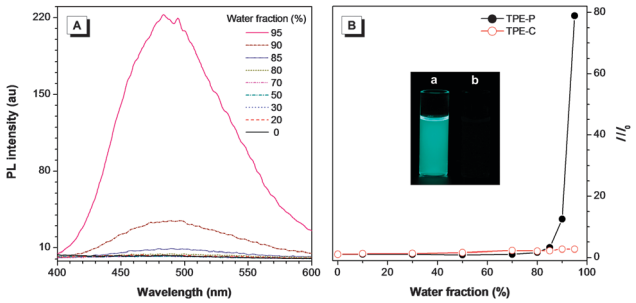


Fig. 1 (A) PL spectra of TPE-P in the THF–water mixture with different water fractions (f_w). (B) The plot of relative PL intensities (I/I_0) *versus* f_w. I_0 are the PL intensities of the dyes in THF solutions at 488 nm; dye concentration: 10 μM; excitation wavelength: 320 nm. Inset: photographs of (a) TPE-P and (b) TPE-C in f_w = 95% excited using a hand-held UV lamp at 365 nm.

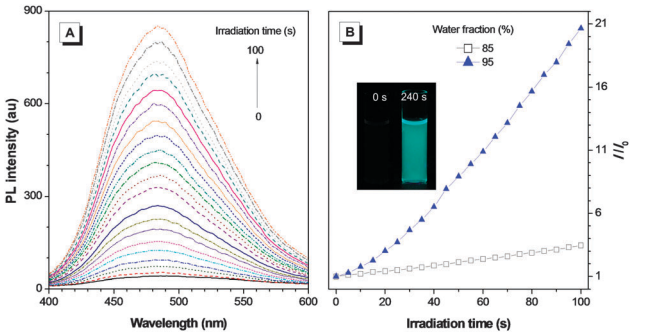


Fig. 2 (A) PL spectra of TPE-C in 95% f_w with different irradiation times. (B) Change in PL intensities of TPE-C at 488 nm in different f_w *versus* irradiation times. Concentration: 10 μM; excitation wavelength: 320 nm. Inset: photographs of TPE-C in 95% f_w excited using a hand-held UV lamp at 365 nm under UV irradiation for 0 s and 240 s.

The synthetic route of TPE-C is depicted in Scheme 2. TPE-P is synthesized *via* Suzuki coupling between 4-bromotetraphenylethene (**1**) and (4-hydroxyphenyl) boronic acid (**2**). The resultant TPE-P is then reacted with 2-nitrobenzyl bromide (**3**) in the presence of Cs_2CO_3 to furnish TPE-C. The structure and purity of the TPE-P and TPE-C are fully characterized by NMR and mass spectrometry (Fig. S10–S17, ESI†).

To investigate the photophysical properties of TPE-C and TPE-P, we firstly conducted UV absorption measurements. The UV spectra of both TPE-C and TPE-P in THF solution exhibit an absorption maximum at 320 nm (Fig. S1, ESI†). We then investigated their photoluminescence (PL) properties. As shown in Fig. 1, both TPE-C and TPE-P are non-fluorescent in pure THF solution. The emission of TPE-P increases swiftly when the water fraction (f_w) in the THF–water mixture exceeds 85%. When f_w = 95%, the PL intensity at 488 nm is 80-fold higher than that in pure THF solution. The fluorescence enhancement of TPE-P is attributed to the formation of nanoaggregates (Fig. S2, ESI†), suggesting that TPE-P is AIE-active.[3] On the other hand, TPE-C remains non-emissive although the nanoaggregates formed when 95% of water was added to the THF solution. The PL results indicated that the emission of TPE-C in the aggregated state is quenched by 2-nitrobenzene through the PeT process.

Inspired by the uncaging process in conventional systems, TPE-C is expected to respond to UV irradiation. As the proposed uncaging mechanism shown in Scheme S2 (ESI†), the 2-nitrobenzyl group in TPE-C is cleaved by UV irradiation and TPE-P and 2-nitrosobenzaldehyde are readily formed.[9] Since TPE-P is highly emissive in the aggregated state, we utilized PL measurements to monitor the uncaging process of TPE-C in the aggregated state. As shown in Fig. 2, TPE-C shows a weak emission in both the THF–water mixtures with f_w = 85% and 95%. Their PL peak intensities at 488 nm gradually enhanced along with the UV irradiation time, indicating that the TPE-P is formed during UV treatment (Fig. 2A and Fig. S3, ESI†). The PL enhancement in f_w = 95% is faster than that in f_w = 85%, this could be because the TPE-P aggregates in 95% water content are more compressed and the intramolecular motions are more restricted (Fig. 2B).[3,4] The photos of TPE-C fluorescence in the THF–water mixture with f_w = 95% taken under UV illumination also demonstrate such an uncaging process (Fig. S4, ESI†).

To further verify whether the cyan fluorescence is attributed to the formation of TPE-P, we conducted high-performance liquid chromatography (HPLC) to monitor the uncaging process. We first ran the pure TPE-P and TPE-C using acetonitrile as the references. The peaks for TPE-P and TPE-C were observed at 1.5 and 2.0 min, respectively (Fig. S5, ESI†). The TPE-C aggregates in the of THF–water mixture with f_w = 95% were then irradiated by UV light and the samples were taken out for HPLC analysis every minute. The HPLC spectra show that the peak area for TPE-C decreases while the peak area for TPE-P increases along with the UV irradiation time (Fig. S6, ESI†), which is consistent with the PL results. As indicated by the mass analysis, the isolated product from HPLC at 1.5 min has an exact mass of 424.1822 (Fig. S7, ESI†), which corresponds to the mass of TPE-P (Fig. S14, ESI†). Based on the above results, it can be concluded that TPE-C is uncaged upon UV irradiation and the released TPE-P accounts for the fluorescence enhancement.

Inspired by rapid and highly efficient release of TPE-P from the caged compound TPE-C in aggregated state, we explored the possibility to utilize TPE-C as a kind of UV activatable fluorescent material for photo-patterning and anti-counterfeiting related applications. First of all, we tried to use filter paper as a substrate for writing. As shown in Fig. S8 (ESI†), the letter "I" is written with TPE-C while the letters "A" and "E" are written with TPE-P for comparison. Before UV treatment, the letters "A" and "E" are highly emissive but the letter "I" is still non-fluorescent. With the increase of UV irradiation time, the emission of letter "I" becomes stronger. Although the emission of letter "I" is still weaker than the letters "A" and "E", it is understandable that the photoactivation process may occur only on the surface of the

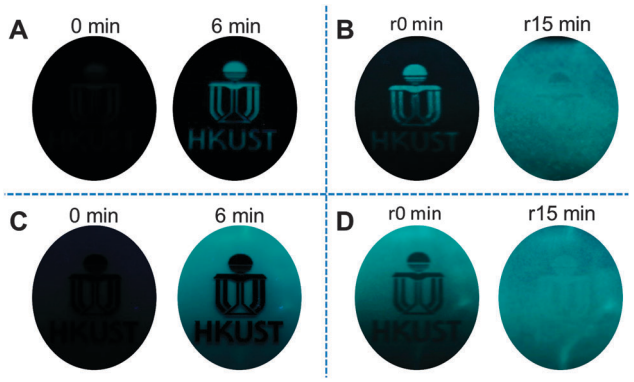


Fig. 3 Photographs of the process of (A and C) photo-patterns by a mask with the HKUST logo under UV irradiation and (B and D) patterns erasing the process after removing the mask under further UV irradiation.

filter paper and most of the TPE-C may not be uncaged. In addition to the fluorescent writing, TPE-C possesses the potential to be used in anti-counterfeiting applications. Since we have demonstrated that the photo-activation can be carried out on the filter paper, we can conveniently fabricate patterns or erase patterns by adding or removing a mask. Filter papers are firstly soaked with the THF solution of TPE-C and dried by using compressed air. Two projector films with the HKUST logo, one a transparent image (Fig. 3A) while the other one a dark image (Fig. 3C), were covered onto the filter papers. The HKUST logo gradually emerged on the filter papers upon UV irradiation. For the film with the transparent logo, the frame structure displays brighter emission than the surroundings. In contrast, the frame structure shows dimmer emission than the surroundings when a mask with a dark logo is used. Moreover, the patterns can be erased by further UV irradiation after removing the masks (Fig. 3B and D). Since the caged fluorophores in both the logo and surrounding areas are activated, the whole filter paper is emissive and the patterns cannot be seen as a result. To demonstrate the flexibility of this method, we used other films with different logos to perform the same experiment (Fig. S9, ESI†). All the frame structures of patterns can be presented and also be erased. These photo-patterning and pattern erasing techniques can be potentially applied for one-time anti-counterfeiting protection, especially for high-valued products.

We have designed and synthesized a new caged fluorophore based on a TPE derivative and a 2-nitrobenzyl group. The caged compound can be photoactivated and induced to emit strong cyan fluorescence in the aggregated state or solid state by UV irradiation. This property of the caged fluorophore enables it to be applied in photo-patterning and anti-counterfeiting related applications. The exploration of biological applications of the caged fluorophore and the synthesis of other caged compounds with AIE moieties with long-wavelength emission are in progress.

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