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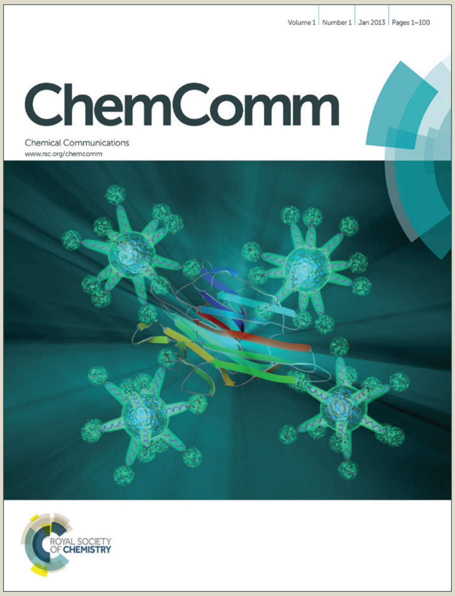

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Tetraphenylethene-based caged compound: synthesis, properties and applications

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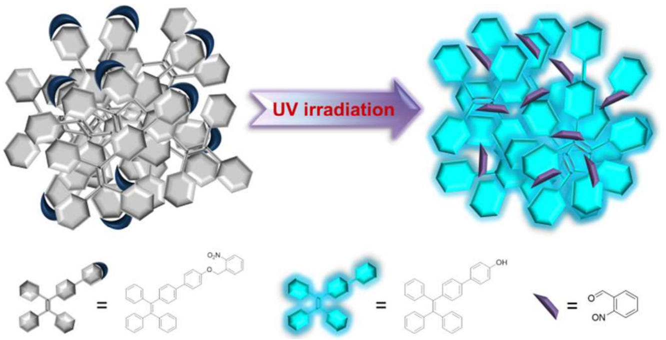
A tetraphenylethene-based caged compound (TPE-C) is designed and synthesized. TPE-C is non-fluorescent either in solution or in aggregated state, but its emission can be induced to emit strong cyan emission in aggregated state by UV irradiation. Such property enables TPE-C to be applied in photo-patterning 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] 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 stimulus 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] 2-Nitrobenzyl group is the most representative quencher for caged fluorophores.[5-9] Because of strong electron-withdrawing ability of 2-nitrobenzyl group, the emission of fluorophore in the caged compound is quenched through photo-induced electron transfer (PeT) process. Once 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 almost completely recovered 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 though a long time UV irradiation because the emission of uncaged fluorophores is quenched by aggregation-caused quenching (ACQ). Such ACQ effect hence has greatly limited the applications of the caged compounds in the aggregated state.

Scheme 1. Uncaging process of TPE-C

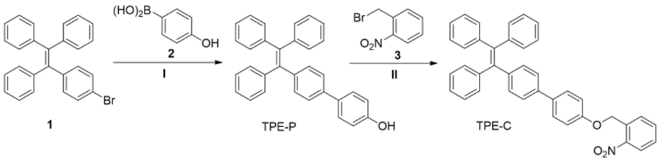


Herein, we reported a new caged compound (TPE-C), which constructed by an AIE-active tetraphenylethene (TPE) derivative as a fluorophore with a 2-nitrobenzene group as a quencher. TPE-C is non-fluorescent either in solution or in aggregated state but its emission in aggregated state can be photoactivated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

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 measurement. 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 mixture of THF/water exceed 85%. When f_w = 95%, the PL intensity at 488 nm is 80-fold higher than that in pure THF solution. The fluorescent 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 have formed when 95% of water is added to the THF solution. The PL results indicated that the emission of TPE-C in aggregated state is quenched by 2-nitrobenzene through PeT process.

Scheme 2. Synthetic route to TPE-P and TPE-C



I: Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, THF/H$_2$O, reflux overnight; II: Cs$_2$CO$_3$, MeCN, 80 °C, 8 h

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, 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 aggregated state, we utilized PL measurements to monitor the uncaging process of TPE-C in aggregated state. As shown in Fig. 2, TPE-C shows a weak emission in both the mixtures of THF/water with f_w = 85% and 95%. Their PL peak intensities at 488 nm are gradually enhanced along with the UV irradiation time, indicating that the TPE-P is formed during UV treatment (Fig. 2A and Fig. S3). The PL enhancement in f_w = 95% is faster than of f_w = 85%, it should 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 fluorescent photos of TPE-C in the mixture of THF/water with f_w = 95% taken under UV illumination also demonstrate such an uncaging process (Fig. S4, ESI†).

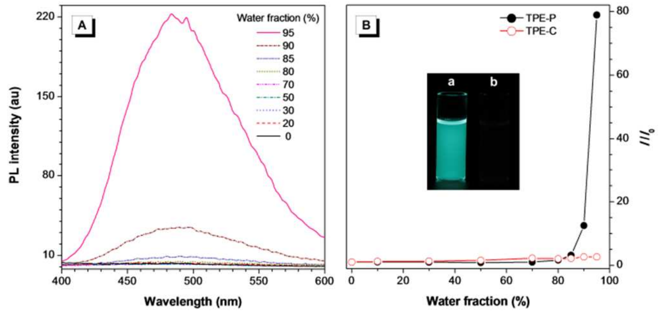


Fig. 1 (A) PL spectra of TPE-P in THF/water mixture with different water fractions (f_w). (B) Plot of relative PL intensities (I/I_0) *versus* f_w. I_0 are the PL intensities at 488 nm of the dyes in THF solutions; Dye concentration: 10 μM; excitation wavelength: 320 nm. Inset: photographs of (a) TPE-P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

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 run the pure TPE-P and TPE-C using acetonitrile as the references. The peaks for TPE-P and TPE-C are observed at 1.5 and 2.0 min, respectively (Fig. S5, ESI†). The TPE-C aggregates in the mixture of THF/water with f_w = 95% are then irradiated by UV light and the samples are taken out for HPLC analysis in every minute. The HPLC spectra show that the peak area for TPE-C is decreasing while the peak area for TPE-P is increasing 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), which corresponds to the mass of TPE-P (Fig. S14, ESI†). Based on the above results, it can conclude that TPE-C is uncaged under UV irradiation and the released TPE-P accounts for the fluorescent enhancement.

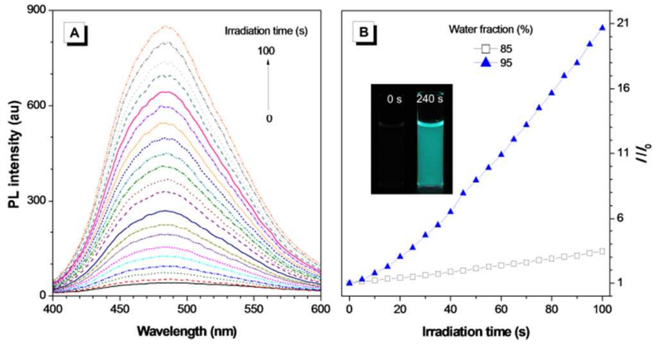


Fig. 2 (A) PL spectra of TPE-C in 95% f_w with different irradiation time. (B) Change in PL intensities at 488 nm of TPE-C in different f_w *versus* irradiation time. Concentration: 10 μM; excitation wavelength: 320 nm. Inset: photographs of TPE-C in 95% f_w excited by hand-held UV lamp at 365 nm under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

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, 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. As 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 only occur on the surface of filter paper and most of the TPE-C has not been 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 compressed air. Two projector films with HKUST logo, one is transparent image (Fig. 3A) while the other one is 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 transparent logo, the frame structure displays brighter emission than the surrounding. On the contrary, the frame structure shows dimmer emission than the surrounding 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 3D). Since the caged fluorophore in both logo and surrounding areas are activated, the whole filter papers are emissive and the patterns cannot be seen as a resulted. To demonstrate the flexibility of this method, we used other films with different logo 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.

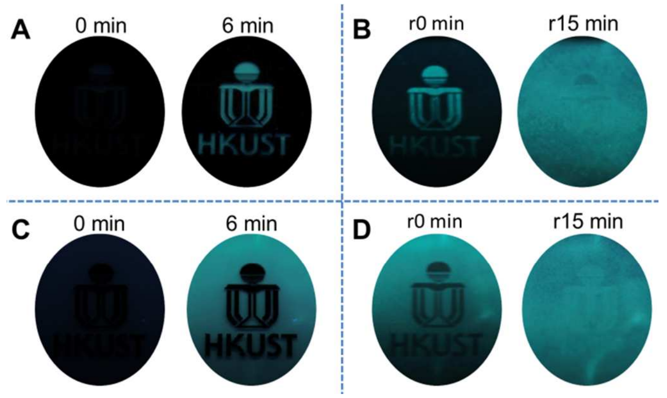


Fig. 3 Photographs of the process of (A and C) photo-pattern by a mask with HKUST logo under UV irradiation and (B and D) pattern erasing process after removing the mask under further UV irradiation.

Conclusion

We have designed and synthesized a new caged fluorophore based on a TPE derivative and 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. Such 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 the progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed synthesis and characterization of TPE-P and TPE-C; UV and PL spectra for TPE-C; photographs of TPE-C under UV irradiation; HPLC of TPE-C with different irradiation times; photo-patterning and pattern erasing. See DOI: 10.1039/c000000x/a

1 (a) *Advanced Concepts in Fluorescence Sensing*, ed. C. D. Geddes and J. R. Lakopwicz, Springer, Norwell, 2005; (b) K. E. Sapsford, L. Berti and I. L. Medintz, *Angew. Chem., Int. Ed.*, 2006, **45**, 4562; (c) S. M. Borisov and O. S. Wolfbeis, *Chem. Rev.*, 2008, **108**, 423; (d) B. N. G. Giepmans, S. R. Adams, M. H. Ellisman and R. Y. Tsien, *Science*, 2006, **312**, 217; (e) M. H. Lim and S. J. Lippard, *Acc. Chem. Res.*, 2007, **40**, 41.

2 (a) F. J. M. Hoeben, P. Jonkheijm, E.W.Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105,** 1491; (b) U.H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605; (c) F. Hide, M. A. Diaz-Garcia, B. J. Schwartz and A. J. Heeger, *Acc. Chem. Res.*, 1997, **30**, 430; (d) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539; (e) B. W. D'Andrade and S. R. Forrest, *Adv. Mater.*, 2004, **16**, 1585.

3 (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, Chem. Commun., 2001, 1740; (b) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (c) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (d) J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang and B. Z. Tang, *Adv. Mater*, 2014, submitted; (e) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu and J. Xu, *Chem. Soc. Rev.*, 2012, **41**, 3878; (f) D. Ding, K. Li, B. Liu and B. Z. Tang, *Acc. Chem. Res.*, 2013, **46**, 2441; (g) M. Wang, G. Zhang, D. Zhang, D. Zhu and B. Z. Tang, *J. Mater. Chem.*, 2010, **20**, 1858.

4 (a) Z. Liu, W. Xue, Z. Cai, G. Zhang and D. Zhang, *J. Mater. Chem.*, 2011, **21**, 14487; (b) L. Peng, M. Wang, G. Zhang, D. Zhang and D. Zhu, *Org. Lett.*, 2009, **11**, 1943; (c) Q. Chen, N. Bian, C. Cao, X.-L. Qiu, A.-D. Qi and B.-H. Han, *Chem. Commun.*, 2010, **46**, 4067; (d) C. W. T. Leung, Y. Hong, S. Chen, E. Zhao, J. W. Y. Lam and B. Z. Tang, *J. Am. Chem. Soc.*, 2013, **135**, 62; (e) S. Chen, J. Liu, Y. Liu, H. Su, Y. Hong, C. K. W. Jim, R. T. K. Kwok, N. Zhao, W. Qin, J. W. Y. Lam, K. S. Wong and B. Z. Tang, *Chem. Sci.*, 2012, **3**, 1804; (f) B. Xu, Z. Chi, X. Zhang, H. Li, C. Chen, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, 2011, **47**, 11080.

5 (a) T. J. Mitchison, K. E. Sawin, J. A. Theriot, K. Gee and A. Mallavarapu, *Methods Enzymol.*, 1998, **291**, 63; (b) M. Fernandez-Suarez and A. Y. Ting, *Nat. Rev. Mol. Cell Biol.*, 2008, **9**, 929; (c) J. C. Politz, *Trends Cell Biol.*, 1999, **9**, 284.

6 T. Kobayashi, T. Komatsu, M. Kamiya, C. Campos, M. Gonzalez-Gaitan, T. Terai, K. Hanaoka, T. Nagano and Y. Urano, *J. Am. Chem. Soc.*, 2012, **134**, 11153.

7 T. Kobayashi, Y. Urano, M. Kamiya, T. Ueno, H. Kojima and T. Nagano, *J. Am, Chem. Soc.*, 2007, **129**, 6696.

8 S. Banala, D. Maurel, S. Manley and K. Johnsson, *ACS Chem. Biol.*, 2012, **7**, 289.

9 Y. V. Il'ichev, M. A. Schworer and J. Wirz, *J. Am. Chem. Soc.*, 2004, **126**, 4581.

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