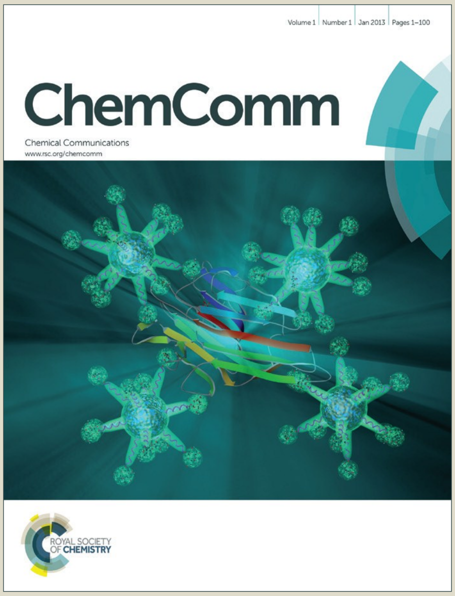
ChemComm

Accepted Manuscript



ChemComm RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

A Fluorescent Turn-on Low Dose Detection of Gamma-Ray Radiation Based on Aggregation-Induced Emission

Xiaobiao Dong, Fang Hu, Zitong Liu, Guanxin Zhang,* Deqing Zhang*

Received 00th January 2012,
Accepted 00th January 2012

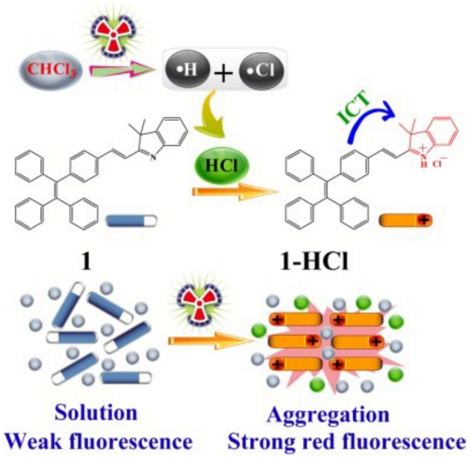
DOI: 10.1039/x0xx00000x

www.rsc.org/

A new sensitive fluorescence turn-on detection of gamma-ray radiation is reported by taking advantage of aggregation induced-emission (AIE) behaviour of tetraphenylethylene unit and the cascade radiochemical and protonation reactions.

Gamma-ray radiation as one kind of ionizing radiation exists in many areas such as nuclear science, medicine, metallurgy, the food industry, and the environment.[1] However, it is well known that gamma-ray radiation can be very hazardous to human health. Currently, the growing violence in terrorist attacks leads to greater awareness of the threat of nuclear and radiological terrorism.[2] Thus, to develop facile and easily-operated methods for sensitive and quick detection of gamma-ray radiation is highly desired and urgent. A number of detection and measurement devices have been invented, [3-9] including mainly ionization chambers, scintillation, and thermoluminescent detectors as well as film badge dosimeters and semiconductor detectors. However, some of these detection methods are required to be operated at low temperature and exhibit low sensitivity to non-charged radiation, and for others the instrumentation is complicated and voluminous. Swager and his coworkers have recently reported a new sensing scheme for gamma-radiation by using a polymer/multiwalled carbon nanotube (MWCNT).[9] But, the detection sensitivity is not high. In fact, low dose detection of gamma-radiation remains essential in medical radiation treatment of cancer and for nuclear relevant security.

Fluorescence detection is characteristic for its sensitivity and easy operation.[10-12] Thus, fluorometry for gamma-ray radiation has caught more attentions recently.[13,14] Some of us reported previously a fluorescence turn-off sensor for gamma-ray radiation by combination of the aggregation-induce emission (AIE) behavior of silole molecules and the fact that polymers with –SO_2 groups in the main chain can be degraded upon gamma-ray radiation.[13a] Zang and his coworkers have very recently described a remarkably sensitive detection of gamma-ray radiation via fluorescence quenching mechanism.[14] Generally, fluorescence turn-on detection is advantageous by considering its high sensitivity and easy-operation. In fact, fluorescence turn-on detection of gamma-ray radiation is still unknown to the best of our knowledge.



Scheme 1. Chemical structures of compound **1** and **1•HCl** and design rationale for the fluorescence turn-on detection of gamma-ray radiation.

In this paper we report a new fluorescence turn-on detection of gamma-ray radiation based on the AIE feature of tetraphenylethylene (TPE) derivatives. The design rationale is illustrated in Scheme 1 and explained as follows: 1) compound **1,** a tetraphenylethylene derivative bearing a conjugated 3,3'-dimethyl-3H-indole, is expected to be soluble in common organic solvents such as $CHCl_3$ and CH_2Cl_2. Thus, it is anticipated that **1** is weakly emissive in these solvents according to previous studies;[15-21] 2) However, the 3,3'-dimethyl-3H-indole unit in **1** can react with HCl easily to afford indolium moiety to generate **1•HCl** (see Scheme 1) which is expected to show low solubility in $CHCl_3$ or CH_2Cl_2; thus, aggregation will occur and the fluorescence of TPE moiety can be switched on based on the AIE feature of TPE molecules. Moreover, the emission is anticipated to be red-shifted owing to the electron-withdrawing effect of indolium moiety in **1•HCl** based on our previous observations.[20b, 21] 3) Under gamma-ray radiation, the halogenated solvents including $CHCl_3$ and CH_2Cl_2 decompose into free radicals. Due to their instability, recombination of these radicals occurs easily to yield some new compounds including hydrochloric acid.[22] Therefore, compound **1** can be employed as a fluorescence turn-on probe for gamma-ray radiation in halogenated solvents including $CHCl_3$ and CH_2Cl_2.

Compound **1** was synthesized *via* the condensation of compound **2**[23] with the 2, 3, 3'-trimethylindolenine (see Scheme S1).The chemical structure of **1** was characterized with ^1H NMR, ^{13}C NMR, and high-resolution ESI-mass spectra (ESI†). As expected, **1** can be well dissolved in common organic solvents including $CHCl_3$ and CH_2Cl_2.

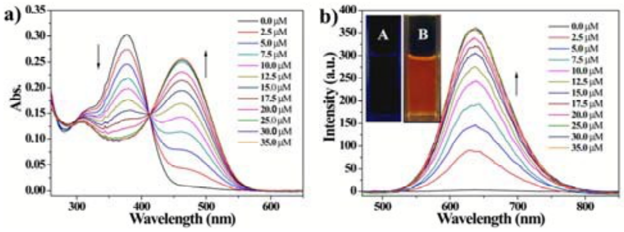


Fig. 1 a) Absorption and b) fluorescence spectra ($\lambda_{ex.}$ = 460 nm) of the $CHCl_3$ solution of **1** (10.0 μM) in the presence of HCl (from 0 to 35.0 μM); inset of Figure 1b shows photos of the solution of **1** (10.0 μM) before (A) and after (B) addition of 35.0 μM of HCl under 460 nm light irradiation.

Firstly, we investigated the variation of absorption and fluorescence spectra upon addition of HCl. Figure 1a shows the absorption spectrum of **1** and those in the presence of different amounts of HCl. It is obvious that **1** exhibited a strong absorption band in the range of 300-450 nm, whereas a new absorption band centered at 460 nm emerged gradually after addition of HCl and the absorption around 378 nm was reduced simultaneously as depicted in Figure 1. The appearance of the new absorption can be attributed to the intramolecular electron donor-acceptor interaction between TPE and indolium that is generated by protonation of 3, 3'-dimethyl-3H-indole unit in **1**.[20b, 21]

As anticipated, the $CHCl_3$ solution of **1** (10 μM) was almost non-emissive in the absence of HCl. However, after addition of HCl the fluorescence intensity at 640 nm of **1** increased gradually as shown in Figure 1b. For instance, the fluorescence intensity at 640 nm increased by more than 100 times when the concentration of HCl reached 25 μM. Indeed, such fluorescence enhancement can be distinguished by naked-eye as shown in the inset of Figure 1b, where photos of solutions of **1** in the absence and presence of HCl under light (460 nm) illumination are displayed. As illustrated in Scheme 1, such fluorescence enhancement is attributed to the protonation of 3,3'-dimethyl-3H-indole in **1** to generate **1•HCl** which is expected to show low solubility in $CHCl_3$ and aggregation occurs accordingly.[24]

The formation of fluorescent aggregates was confirmed by confocal laser scanning microscopic (CLSM), scanning electron microscopic (SEM) and dynamic light scattering (DLS) studies. As displayed in Figures S2 and S3, there were almost no fluorescent aggregates for the solution of **1** before the addition of HCl; however, fluorescent aggregates emerged after addition of HCl based on the CLSM and SEM images. DLS data (see Figure S4a) also indicated the formation of aggregates of ca. 60 nm for the solution of **1** (10.0 μM) after addition of HCl (35 μM).

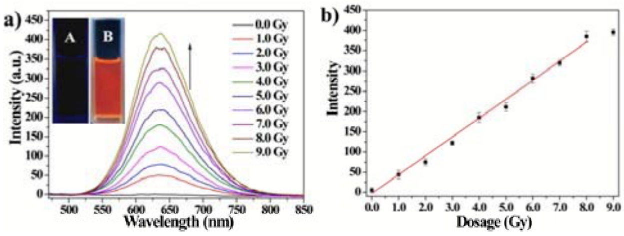


Fig. 2 a) Fluorescence spectra ($\lambda_{ex.}$ = 460 nm) of the $CHCl_3$ solution of compound **1** (3.0 mL, 10.0 μM) recorded under increasing dosages of gamma-ray radiation up to 9.0 Gy; inset shows photos of the solution of **1** (10.0 μM) before (A) and after (B) gamma-ray radiation under 460 nm light irradiation. b) A plot showing the fluorescence intensity at 640 nm *vs.* the dosage of gamma-ray radiation for the $CHCl_3$ solution of **1** (3.0 mL, 10.0 μM); the data in the range of 0.0-8.0 Gy were fitted with the following equation: Y= 46.37351X-6.48515, R^2 = 0.991.

In the following, we will demonstrate the application of **1** for the detection of gamma-ray radiation. As reported previously, halogenated solvents exposed to gamma-ray radiation can be decomposed into various radicals, including hydrogen and chlorine, which then combine to produce hydrochloric acid (HCl).[22] Therefore, it is anticipated that compound **1** can be utilized for the detection of gamma-ray radiation by taking advantage of the cascade radiochemical and protonation reactions. The solutions of **1** (10.0 μM) in $CHCl_3$ were irradiated with different dosages of gamma-ray radiation. Then, the fluorescent and absorption spectra of each solution were measured as shown in Figure 2 and Figure S5. Both the absorption and fluorescence spectra of **1** after irradiated by gamma-ray radiation underwent almost identical spectral change as those for **1** upon addition of HCl (see Figure 1). As expected, red emission was observed when the solution radiated with gamma-ray irradiation (see inset of Figure 2a). As depicted in Figure 2a, the fluorescent intensity of **1** increased gradually with the increasing dosage of gamma-ray radiation.[25] For instance, the fluorescence intensity of **1** at 640 nm was enhanced by more than 100 times when the dosage reached 8.0 Gy. As shown in Figure S5E, the fluorescence intensity of **1** became saturated when the $CHCl_3$ solution was exposed to 12.0 Gy of gamma-ray irradiation.[26] Figure 2b shows the variation of fluorescence intensity of **1** at 640 nm as the function of dosage of gamma-ray radiation. As depicted in Figure 2b, the $CHCl_3$ solution of **1** can be utilized to detect gamma-ray radiation with dosage as low as 1.0 Gy, which is the lowest dosage with our gamma-radiation source. Note that the solution of **1** is more sensitive toward gamma-ray radiation than most of the reported sensing system.[9,13] Interestingly, the fluorescence intensity increased almost linearly with the dosage of gamma-ray radiation in the range of 0.0–8.0 Gy. Based on this linear relation, the limit of detection of **1** for gamma-ray radiation was estimated to be 0.023 Gy.

Such fluorescence enhancement was also ascribed to i) the protonation of **1** by HCl that was formed after gamma-ray radiation and ii) the aggregation of **1•HCl** in $CHCl_3$. In fact, red fluorescent aggregates were detected for the $CHCl_3$ solution of **1** after gamma-ray irradiation (dosage = 8.0 Gy) with CLSM and SEM as shown in Figure 3 and Figure S3. Moreover, DLS studies manifested that aggregates with size around 110 nm were formed in the $CHCl_3$ solution of compound **1** (10.0 μM) after gamma-ray irradiation (see Figure S4b). In comparison, almost no aggregates were observed based on the DLS data (see Figure S4b) before exposed to gamma-ray radiation.

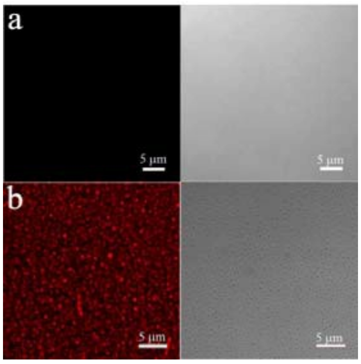


Fig. 3 Fluorescence confocal laser scanning images of **1** (3 mL, 10.0 μM) before (a) and after (b) gamma-ray radiation (dosage = 8.0 Gy); the scale bar represents 5.0 μm.

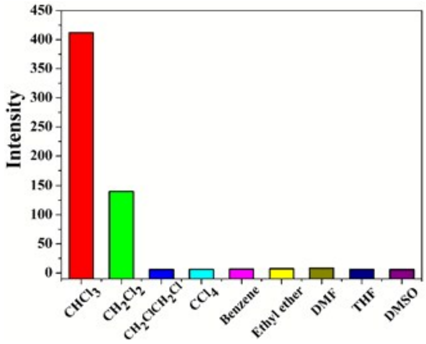


Fig. 4 Variation of fluorescence intensity of **1** (10.0 μM) at 640 nm in different organic solvents after gamma-ray irradiation (dosage = 9.0 Gy); the excitation wavelength was 460 nm, and the concentration of **1** was 10.0 μM in $CHCl_3$ CH_2Cl_2, 1, 2-dichloroethane, CCl_4 and 100.0 μM in benzene, ethyl ether, DMF, DMSO and THF.

To further prove the important role of the halogenated solvents in the radiation induced fluorescence enhancement of **1**, the same experiments were conducted in CH_2Cl_2, 1, 2-dichloroethane, CCl_4 and non-halogenated solvents including benzene, ethyl ether, DMF, DMSO and THF. As depicted in Figure 4, fluorescence enhancement was also observed for **1** in CH_2Cl_2 after gamma-ray radiation, but the degree of fluorescence enhancement was smaller compared to that in $CHCl_3$. However, no detectable fluorescence enhancement was detected for **1** in 1, 2-dichloroethane, CCl_4 and non-halogenated solvents. This observation further supports the hypothesis that the sensing of **1** toward gamma-ray radiation relies on the radiation induced generation of HCl.[27]

In summary, we report a facile and convenient fluorescence turn on detection of gamma-ray radiation based on compound **1**. This new method is designed by the combination of AIE behaviour of TPE compounds and the fact that $CHCl_3$ can be degraded upon gamma-ray radiation to form HCl which will protonate **1** and result in aggregation. This fluorometric turn-on detection of gamma-ray radiation possesses the following features: 1) compound **1** is easily synthesized; 2) the limit of detection for gamma-ray radiation is as low as 0.023 Gy; thus the solution of **1** is much more sensitive toward gamma-radiation; 3) the solution of **1** after exposure to gamma-radiation can be distinguished with naked eyes.

Acknowledgements

This work is supported by grants from National Natural Science Foundation of China, Ministry of Science and Technology of China and Chinese Academy of Sciences.

Notes and references

Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: dqzhang@iccas.ac.cn.

Electronic Supplementary Information (ESI) available: synthesis and characterization of compound **1**, fluorescent image, UV spectra, DLS data and relevant data for compound **1,** See DOI: 10.1039/b000000x/

1 (a) G. Knoll, *Radiation Detection and Measurement*, Wiley-VCH, New York, 1979; (b) R. H. Herz, *The Photographic Action of Ionizing Radiations*, Wiley-Interscience, London, 1969.

2 R. Sarkar, B. Chatterjee, B. Roy, S. Roy, *Rad. Phys. Chem.*, 2006, **75**, 2186.

3 V. S. Kortov, *Rad. Meas.*, 2010, **45**, 512.

4 S. Del Sordo, L. Abbene, E. Caroli, A. M. Mancini, A. Zappettini, P. Ubertini, *Sensors*, 2009, **9**, 3491, and further references within.

5 H. Yücel, A. Solmaz, E. Köse, D. Bor, *App. Radiation and Isotopes*, 2010, **68**, 1040.

6 M. Foxe, G. Lopez, I. Childres, R. Jalilian, C. Roecker, J. Boguski, I. Jovanovic, Y. Chen, *2009 IEEE Nuclear Science Symposium Conference Record*, 2009, N05-1.

7 (a) R. Runkle, L. Smith, A. Peurrung, *J. Appl. Phys.*, 2009, **106**, 041101; (b) G. Fedorov and S. Tereshchenko, *Meas. Tech.*, 1996, **39**, 965; (c) A. Owens, *J. Synchrotron Radiat.*, 2006, **13**, 143.

8 (a) J. Webster, *The Measurement, Sensors and Instrumentation Handbook*, CRC, 1999; (b) S. Graham, R. Friend, S. Fung and S. Moratti, *Synth. Met.*, 1997, **84**, 903.

9 J. Lobez, T. Swager, *Angew. Chem. Int. Ed.*, 2010, **49**, 95.

10 (a) L. Yuan, W. Lin, K. Zheng, L. He, W. Huang, *Chem. Soc. Rev.*, 2013, **42**, 622; (b) J. Du, M. Hu, J. Fan, X. Peng, *Chem. Soc. Rev.*, 2012, **41**, 4511; (c) X. Chen, X. Tian, I. Shin, J. Yoon, *Chem. Soc. Rev.*, 2011, **40**,

4783; (d) H. Kim, Z. Guo, W. Zhu, J. Yoon, H. Tian, *Chem. Soc. Rev.*, 2011, **40**, 79.

11 (a) A. Zucchero, P. McGrier, U. Bunz, *Acc. Chem. Res.*, 2010, **43**, 397; (b) X. Li, X. Gao, W. Shi, H. Ma, *Chem. Rev.*, 2014, **114**, 590; (c) L. Yuan, W. Lin, K. Zheng, S. Zhu, *Acc. Chem. Res.*, 2013, **46**, 1462.

12 (a) X. Qian, Y. Xiao, Y. Xu, X. Guo, J. Qian, W. Zhu, *Chem. Commun.*, 2010, **46**, 6418; (b) H. Zheng, X. Zhan, Q. Bian, X. Zhang, *Chem. Commun.*, 2013, **49**, 429; (c) W. Shi, H. Ma, *Chem. Commun.*, 2012, **48**, 8732; (d) X. Lou, D. Ou, Q. Li, Z. Li, *Chem. Commun.*, 2012, **48**, 8462; (e) M. Jun, B. Roy, K. Ahn, *Chem. Commun.*, 2011, **47**, 7583. (f) M. Xu, J. Han, Y. Zhang, X. Yang, L. Zang, *Chem. Commun.*, 2013, **49**, 11779; (g) L. Yuan, W. Lin, Y. Yang, H. Chen, *J. Am. Chem. Soc.,* 2012, **134**, 1200.

13 (a) Z. Liu, W. Wang, Z. Cai, G. Zhang, D. Zhang, *J. Mater. Chem.*, 2011, **21**, 14487; (b) E. Bronze-Uhle, A. Batagin-Neto, F. Lavarda, C. Graeff, *J. Appl. Phys.*, 2011, **110**, No. 073510; (c) A. Singh, K. Chen, S. Adelstein, A. Kassis, *Radiat. Res.* 2007, **168**, 233.

14 J. Han, M. Xu, B. Wang, N. Wu, X. Yang, H. Yang, B. Salter, L. Zang, *J. Am. Chem. Soc.,* 2014, **136**, 5090.

15 A. Qin, B. Tang, *Aggregation-Induced Emission: Fundamentals and Applications*, Wiley, New York, 2013.

16 (a) D. Ding, K. Li, B. Liu, B. Tang, *Acc. Chem. Res.* 2013, **46**, 2441; (b) J. Zhang, Q. Zou, H. Tian, *Adv. Mater.*, 2013, **25**, 378; (c) M. Wang, G. Zhang, D. Zhang, D. Zhu and B. Tang, *J. Mater. Chem.*, 2010, **20**, 1858; (d) Y. Hong, J. Lam, B. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (e) G. Zhang, F. Hu, D. Zhang, *Langmuir*, DOI: 10.1021/la5029367

17 (a) C. Leung, Y. Hong, J. Hanske, E. Zhao, S. Chen, E. Pletneva, B. Tang, *Anal. Chem.* 2014, **86**, 1263; (b) M. Raju, H. Lin, *Org. Lett.*, 2014, **16**, 5564; (c) Y. Guo, X. Feng, T. Han, S. Wang, Z. Lin, Y. Dong, B. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 15485; (d) X. Wang, J. Hu, G. Zhang, S. Liu, *J. Am. Chem. Soc.*, 2014, **136**, 9890; (e) P. Galer, E. C. Korošec, M. Vidmar, B. Šket, *J. Am. Chem. Soc.*, 2014, **136**, 7383.

18 (a) X. Wu, X. Sun, Z. Guo, J. Tang, Y. Shen, T. James, H. Tian, W. Zhu, *J. Am. Chem. Soc.,* 2014, **136**, 3579; (b) Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie, H. Tian, *Angew. Chem. Int. ed.*, 2011, **50**, 11654; (c) J. Huang, Y. Jiang, J. Yang, R. Tang, N. Xie, Q. Li, H. Kwok, B. Tang, Z. Li, *J. Mater. Chem. C*, 2014, **2**, 2028. (d) X. Shen, Y. Wang, H. Zhang, A. Qin, J. Sun, B. Tang, *Chem. Commun.*, 2014, **50**, 8747; (e) Q. Chen, N. Bian, C. Cao, X. Qiu, A. Qi, B. Han, *Chem. Commun.*, 2010, **46**, 4067.

19 (a) A. Shao, Z. Guo, S. Zhu, S. Zhu, P, Shi, H. Tian, W. Zhu, *Chem. Sci.*, 2014, **5**, 1383; (b) C. Ma, B. Xu, G. Xie, J. He, X. Zhou, B. Peng, L. Jiang, B. Xu, W. Tian, Z. Chi, S. Liu, Y. Zhang, J. Xu, *Chem. Commun.*, 2014, **50**, 7374; (c) S. Song, H. Zheng, D. Li, J. Wang, H. Feng, Z. Zhu, Y. Chen, Y. Zheng, *Org. Lett.*, 2014, **16**, 2170; (d) J. Tong, Y. Wang, J. Mei, J. Wang, A. Qin, J. Sun, B. Tang, *Chem. Eur. J.*, 2014, **20**, 4661; (e) Y. Cai, L. Li, Z. Wang, J. Sun, A. Qin, B. Tang, *Chem. Commun.* 2014, **50**, 8892.; (f) J. Huang, N. Sun, P. Chen, R. Tang, Q. Li, D. Ma, Z. Li, *Chem. Commun.,* 2014, **50**, 2136.

20 (a) W. Chen, Q. Li,W. Zheng, F. Hu, G. Zhang, Z. Wang, D. Zhang, X. Jiang, *Angew. Chem. Int. Ed.*, 2014, **53**, 13734; (b) F. Hu, Y. Huang, G. Zhang, R. Zhao, H. Yang, D. Zhang, *Anal. Chem.*, 2014, **86**, 7987. (c) Y. Huang, F. Hu, R. Zhao, G. Zhang, H. Yang, D. Zhang, *Chem. Eur. J.*, 2014, **20**, 158; (d) M. Wang, X. Gu, G. Zhang, D. Zhang, D. Zhu, *Anal. Chem.*, 2009, **81**, 4444; (e) X. Huang, X. Gu, G. Zhang, D. Zhang, *Chem. Commun.*, 2012, **48**, 12915.

21 (a) X. Gu, J. Yao, G. Zhang, C. Zhang, Y. Yan, Y. Zhao, D. Zhang, *Chem. Asian J.,* 2013, **8**, 2362; (b) F. Hu, G. Zhang, C. Zhan, W. Zhang, Y. Yan, Y. Zhao, H. Fu, D. Zhang, *Small*, DOI: 10.1002/smll.201402051.

22 (a) M. Ottolenghi, G. Stein, *Radiat. Res.,* 1961, **14**, 281; (b) H. Werner, R. Firestone, *J. Phys. Chem.* 1965, **69**, 840.

23 X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu, Y. Zhang, J. Xu, *Chem. Asian J.,* 2011, **6**, 808.

24 As depicted in Figure S1, acetic acid, trifluoroacetic acid and trifluoromethanesulfonic acid can also induce the fluorescence enhancement of **1**. The results further manifest that such fluorescence enhancement is caused by protonation of 3,3'-dimethyl-3H-indole in **1**.

25 The dosages were dependent on the periods during which the solutions were exposed to the gamma-ray radiation source. Therefore, the fluorescence intensity is affected by the exposure time. Longer exposure time will yield more HCl, accordingly much stronger red fluorescence will occur. The exposure times were 38 s, 93 s, 148 s, 203 s, 257 s, 312 s, 367 s, 422 s, 477s and 641 s, corresponding to dosages of 1.0 Gy, 2.0 Gy, 3.0 Gy, 4.0 Gy, 5.0 Gy, 6.0 Gy, 7.0 Gy, 8.0 Gy, 9.0 Gy and 12.0 Gy, respectively. The dosage data were verified with Alanine Dosimeters (dose range: 1 Gy-200 kGy).

26 The dosage of gamma-ray irradiation needed for the solution of **1** (3.0 mL) to become saturated is dependent on the concentration of **1**. As shown in Figure S5, the maximum fluorescence intensity was yielded for the $CHCl_3$ solution of **1** (3.0 mL, 5.0 μM) after it was exposed to 6.0 Gy of gamma-ray irradiation. When the concentration of the solution increased to 20.0 μM, the fluorescence intensity became saturated after exposure to 15.0 Gy of gamma-ray radiation.

27 The difference of fluorescence enhancement observed for **1** in $CHCl_3$, CH_2Cl_2 and 1, 2-dichloroethane after gamma-ray radiation might be caused by their different carbon-hydrogen bond energies. For example, the bond energy (95.8 kcal/mol) of carbon-hydrogen bond in $CHCl_3$ is lower than that of carbon-hydrogen bond (100.6 kcal/mol) in CH_2Cl_2 (see R. Weast, *CRC Handbook of Chemistry and Physics* (70th ed.), CRC Press, Florida). Thus, the decomposition reaction of $CHCl_3$ can occur more easily than that of CH_2Cl_2. As CCl_4 contains no hydrogen, HCl cannot be generated after gamma-ray radiation. Similarly, HCl cannot be produced after exposure of non-halogenated solvents to gamma-radiation. These agree with the observation that no fluorescence enhancement was not observed for **1** in CCl_4 and non-halogenated solvents after gamma-ray radiation.