# **Dose Measurement in Food Irradiation**

# Development of Fluorescence Gamma Dosimeters

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ABSTRACT

We have developed two fluorescent  $\gamma$ -dosimeters based on BODIPY dyes. In one case, 8-anilino BODIPY was used which showed "off-on" fluorescence under g-exposure with dynamic range of 0-100 Gy. On the other hand, 8-(N,N-dimethyanilino) BODIPY based dosimeter showed ratiometric "off-on" fluorescence enhancement applicable in the range of 0-150 Gy with limit of detection (LOD) of 0.5 Gy. These highly sensitive fluorescence dosimeters will be useful for absorbed dose measurement in food irradiation processes.

Change in absorption of anilino-Boron Dipyrromethene (BODIPY) dye in CHCl<sub>3</sub> under y-irradiation exposure of increasing doses

KEYWORDS: Dosimeter, Gamma radiation, Low dose, Bodipy dyes, Sensitivity, Colourimetric and Fluorometric measurement

# Introduction

Gamma ( $\gamma$ ) is highly ionizing radiation, thus a very low dose  $\gamma$ -radiation can cause serious harm to the living biological systems. Thus, detection of gamma radiation is highly important to protect the lives [1]. Also, various safe uses of the gamma radiation are known like food, blood and sludge irradiation, radio-imaging and therapy, medical equipment sterilizations etc [2]. For all these applications, different doses of gamma radiation are being used which required to be precise to protect the materials and lives. Thus, accurate dosimeters are in high demands.

Conventional gamma-ray detectors like ionization chambers, scintillators and semiconductor detectors suffer from various limitations such as bulkiness, lack of sensitivity, high costs, inability to provide real-time three-dimensional data etc. [1,3]. Different dosimeters such as Fricke, clear poly(methyl methacrylate) (PMMA), dyed PMMA and radiochromic film dosimetry along with various luminescent dosimeters like TLD, RPLD, OSLD are also known for gamma dose measurements [1,4]. But they also have various limitations like low sensitivity and accuracy, dose range, anomalous fading, change in sample properties in repeated uses etc. Thus, detection of  $\gamma$ -radiations especially low dose gamma radiation is a real challenge. As a result, there is an urgent need for the development of simpler, highly sensitive and cost-effective gamma-ray detection systems.

Uses of fluorescence techniques are highly popular in chemical and biological sensors due to its high sensitivity, low cost, easy operation etc. But its use in  $\gamma$ -radiation detection is not very known so far [5-8]. We envisaged that use of fluorescence technique could be highly useful for the development of the low dose gamma dosimeters. For the current studies, we have chosen two anilino-Boron Dipyrromethene (BODIPY) dyes (1, 2) (Fig.1(a)). Their synthesis, photophysical and gamma dosimetry studies are discussed below.

### **Materials and Methods**

BODIPY dyes 1-2 were synthesized by using the previously reported methods [8]. Dye 1-2 in chloroform



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Fig.1: (a) Chemical structures of the anilino-BODIPY dyes (1,2). (b) Absorption and fluorescence spectra of dye 2 in absence and presence of acid.



Fig.2: (a) Change in absorption of dye 1 in  $CHCl_3$  under  $\gamma$ -irradiation exposure of increasing doses. Inset: Change in colour of the solution after 100 Gy  $\gamma$ -exposure. (b) Change in fluorescence spectra of dye 1 in  $CHCl_3$  under  $\gamma$ -irradiation exposure of increasing doses. Inset: Plot of fluorescence intensity changes with  $\gamma$ -irradiation doses and colour change of the solution after 100 Gy  $\gamma$ -exposure.

(~10<sup>-6</sup> M, 2 ml) were exposed with specified gamma radiation doses using the Blood Irradiator 2000 (Sr. No.14; Dose rate: 0.386 Gy/min; Source: <sup>60</sup>Co) and Blood Irradiator 2000 (Sr. No.48; Dose rate: 5.794 Gy/min; Source: <sup>60</sup>Co) (Make: Board of Radiation and Isotope Technology (BRIT), DAE, Mumbai, India). Then the absorbance and fluorescence of the solutions were recorded after 10 min.

# **Results and Discussion**

Photophysical properties of the dyes 1-2 were evaluated in chloroform. Dye 1 showed narrow absorption with  $\lambda_{abs}$  at 497 nm and low fluorescence with  $\lambda_n$  at 522 nm. While dye 2 showed absorption band with  $\lambda_{abs}$  at 496 nm and very week fluorescence ( $\lambda_n$  = 609 nm). Both the dyes are low-fluorescent in organic solvent due to the photo-induced electron transfers of the nitrogen lone pairs to the BODIPY core. In presence of acids, this nitrogen lone pairs are blocked by the H<sup>+</sup> ion, thus both the anilino-BODIPY dyes became fluorescent [9].For example, in presence of acid, dye 1 showed slightly red shifted absorption spectra ( $\lambda_{abs}$  = 503 nm) with enhanced greenish fluorescence. Similarly, for dye 2,  $\lambda_{abs}$  is red shifted by 11 nm with highly enhanced greenish yellow fluorescence (Fig.1(b)). Thus, both the dyes are capable of sensing acids. Under  $\gamma$ -exposure, chloroform produced hydride and chloride radicals

which generate HCl after recombination [8]. Thus, detection of HCl in  $\gamma$ -exposed chloroform can be used for sensing of  $\gamma$ -radiation. This prompted us to check the gamma sensing abilities of the dyes 1-2 in chloroform.

Upon  $\gamma$ -exposure with increasing doses, absorption of dye 1 started decreasing with slight red shift in  $\lambda_{abs}$  (5 nm). Yellow coloured solution changed to faint yellow after 100 Gy of  $\gamma$ -exposure. The fluorescence peak at 522 nm increases gradually upto 100 Gy and the then saturated. Thus, due to this "off-on" fluorescence sensing, very low yellowish fluorescence converted to intense greenish-yellow. Intensity of  $\lambda_{\rm n}$  (522 nm) enhanced by 5 folds under 100 Gy of  $\gamma$ -irradiation. Therefore, this dosimeter is useful for  $\gamma$ -radiation detection in the range of 0-100 Gy

Then,  $\gamma$ -radiation sensing ability of dye 2 was checked. Under  $\gamma$ -exposure, the  $\lambda_{abs}$  of dye 2 was red shifted (11 nm) and the colour of the solution changes from purple to orange colour. The fluorescence peak at 530 nm enhances sharply (100 folds) with decrease in 609 nm peak showing change in the low reddish fluorescence to intense greenish-yellow upon 200 Gy of  $\gamma$ -radiation exposure. Thus, this "off-on" ratiometric change in fluorescence can be used for the measurement of the gamma doses. The fluorescence intensity ratio,  $I_{s30}/I_{e09}$  is



Fig.3: (a) Change in absorption of dye 2 in CHCl<sub>3</sub> under  $\gamma$ -irradiation exposure of increasing doses. Inset: Change in colour of the solution after 200 Gy  $\gamma$ -exposure and and HCl fumes exposure. (b) Change in fluorescence spectra of dye 2 in CHCl<sub>3</sub> under  $\gamma$ -irradiation exposure of increasing doses. Inset: Fluorescence intensity ratio ( $I_{530}$  nm/ $I_{609}$  nm) changes with  $\gamma$ -irradiation doses and colour change of the solution after 200 Gy  $\gamma$ -exposure. Reproduced with permission from ref. [9]. Copyright: Royal Society of Chemistry.

linearly increases upto 150 Gy of gamma doses before it reaches saturation. Thus, the dosimeter can be used in the range of 0-150 Gy with a limit of detection (LOD) of 0.5 Gy. Thus, the new dosimeter is highly sensitive as compared to commonly used absorption based Fricke dosimeter (LOD: 20 Gy). Also, unlike the Fricke dosimeter, response of the newly developed dosimeters does not depend on non-fluorescent impurities [10]. Thus, this anilino-BODIPY based dosimeter will be useful for the absorbed dose measurement in food irradiation processes.

#### Conclusions

Thus, two "off-on" fluorescent dosimeters were developed with dynamic range of 0-100 Gy and 0-150 Gy. These dyes are highly sensitive and easy to use. Thus, these newly developed dosimeters can be used for absorbed dose measurement in  $\gamma$ -irradiation of food materials (sprouting inhibition).

#### Acknowledgements

This work is supported by Department of Atomic Energy, Govt. of India.

## References

[1] G.F. Knoll, Radiation Detection and Measurement, Wiley, New York, 2010.

[2] P.B. Roberts, Radiat. Phys. Chem., 105 (2014) 78-82.

[3] J.G. Webster, Measurement, Instrumentation, and Sensors: Handbook, CRC Press, Boca Raton, FL, 1999.

[4] T. Yanagida, G. Okada, T. Kato, D. Nakauchi and N. Kawaguchi, Radiat. Meas., 158 (2022) 106847.

[5] Z. Liu, W. Xue, Z. Cai, G. Zhang and D. Zhang, J. Mater. Chem., 21 (2011) 14487-14491.

[6] J.-M. Han, M. Xu, B. Wang, N. Wu, X. Yang, H. Yang, B. J. Salter and L. Zang, J. Am. Chem. Soc., 136 (2014) 5090-5096.

[7] X. Dong, F. Hu, Z. Liu, G. Zhang and D. Zhang, Chem. Commun., 51 (2015) 3892-3895.

[8] Choudhary, M. K.; Gorai, S.; Patro, B. S. and Mula, S. ChemPhotoChem, 8 (2024) e202300245.

[9] Choudhary, M. K. and Mula, S. New J. Chem., 47 (2023) 9045-9049.

[10] Dosimetry for Food Irradiation, Technical Reports Series No. 409, IAEA, Vienna, 2002.