Photochemistry and Mechanism Study of Coumarin-3-carboxylic Acid as a PhotoCORM

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Coumarins belong to a large family of chemically active compounds. They are widely found in nature, and thousands of coumarin derivatives have been isolated or synthesized up to now. Coumarin derivatives exhibit diverse biological activities, such as anticancer, antioxidant, or antibacterial effects.¹ In addition, the photochemical properties of coumarins have also extensively been explored and utilized in optical bleaching agents, fluorescent sensors, and photosensitizers.²

In the past decade, therapeutic effects of carbon monoxide (CO) in biological tissues have extensively been studied. The light-triggered CO liberation from CO releasing molecules (photoCORMs) is one of the most promising ways, providing a high temporal and spatial release control. Two promising photoCORMs based on xanthene and BODIPY (Figure 1a and b, respectively) chromophores have been designed and studied recently by our group.³

To understand the mechanism of CO release, we decided to use a coumarin moiety as a simplification of the xanthene photoCORM (a) to extensively study the mechanism of CO release under different experimental conditions.

Herein, the photochemistry of coumarin-3-carboxylic acid (Figure 1c) as a potential photoCORM has been investigated. Our study includes the determination of CO release after irradiation at 355 or 420 nm in acetonitrile and methanol. The details about this reaction and the proposed mechanisms of photolysis will be discussed.



Figure 1. Structure of photoCOMRs based on a) xanthene, b) BODIPY, c) coumarin-3carboxylic acid.

- 2. (a) Pereira, T. M., et al. Curr. Topics. Med. Chem. 2018, 18, 124-148.
 (b)Kasperkiewicz, K., et al. Lett. Drug. Des. Discovery 2016, 13, 465-474.
- 3. (a) Palao E., et al. J. Am. Chem. Soc. 2016, 138, 126-133.

^{1. (}a) Duxia, C., et al. Chem. Rev. 2019, 119 (18), 10403-10519.

⁽b) Yasameen, A., et al. Sys Rev Pharm. 2017, 8 (1), 24-30.

⁽b) Lovely Angel P. A., et al. Org. Lett. 2013, 15, 4552-4555.