2-6-10. Chemiluminescence

Overview

Chemiluminescence (CL) is a phenomenon in which a product in an electronically excited state is produced by a chemical reaction and emits photon. CL includes bioluminescence (BL) of light-emitting organisms such as a firefly with an enzymatic reaction. CL has a long research history and still provides active research subjects for luminescence analyses in the fields of materials and life sciences, because CL can be easily and sensitively detected with a simple instrument made up by a photon-detector and a black box. Thus, syntheses of new CL compounds and mechanistic studies steadily make progress.

Current Status and Frontiers

CL research has been developed since the discovery of CL of lophine (Fig. 1) in the 1870s. Current representative CL compounds are luminols, oxalate esters, and 1,2-dioxetanes (Fig. 1). CL of 1,2-dioxetanes has already been described in Section "1-12-1. Dioxetanes" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0211201.pdf Unlike a fluorescence analysis, which requires excitation light, a CL analysis enables low-background photon-detecting method with a simple device made up by a photon-detector and a black box. In particular, CL is useful for real time imaging analyses, then CL is widely applied in the fields of materials and life sciences. Some recent studies contributing to the development of CL chemistry are presented as follows.

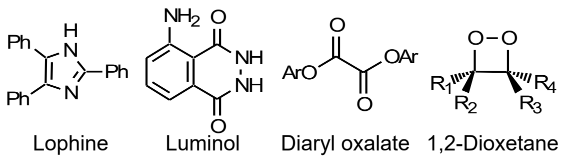

Figure 1. Representative CL compounds.

1. A development of functional 1,2-dioxetanes

A 1,2-dioxetane shows CL by its thermolysis to give an excited carbonyl product. An analytical application of a 1,2-dioxetane was extensively expanded by the development of compound **A** in the 1980s (Fig. 2). When the OH group of **A** is protected by a protecting group (PG), deprotection of PG gives the phenolate anion of **A**, which is much more labile than **A** to lead the fast CL reaction. Thus, the deprotection inducing CL provides a useful way of an analytical application. In addition, the phenolate anion of **A** is a typical highly efficient CL compound. In recent years, the improvement of the **A**-structure for the use in aqueous solutions is in progress. In Japan, bicyclic dioxetanes such as **B** (Fig. 3) were created based on the **A**-structure, to give various derivatives showing characteristic CL properties

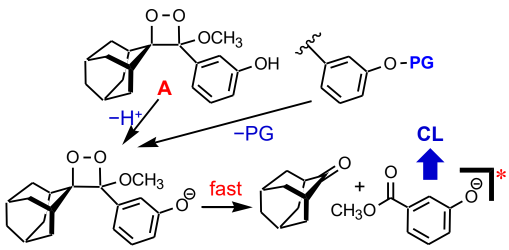

Figure 2. CL of a 1,2-dioxetane **A**.

(Matsumoto, Watanabe et al.).

2. CL-active polymers with a mechanical stimuli-responsivity

Adox (Fig. 3) is a stable 1,2-dioxetane derivative and has been used as a mechanophore in polymer chains (Sijbesma et al.). CL-active polymers with an Adox moiety have contributed to the elucidation of damage mechanisms and the development of high-strength polymers.

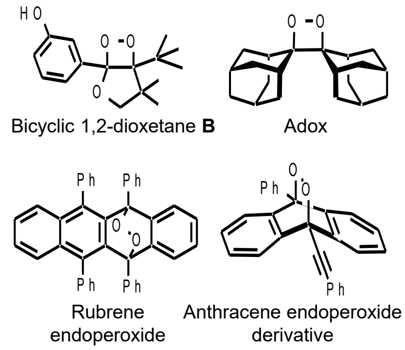

Figure 3. Organic peroxides for CL.

3. CL in the crystalline state

Solid-state CL was discovered in the 1920s with oxygenated rubrene (Fig. 3), but such studies have come into the spotlight recently. First, Matsumoto et al. discovered the unique CL characteristics of bicyclic dioxetanes in crystals. Furthermore, the relationship between reaction control factors, kinetics, phase change, and reactivity is being elucidated with dioxetane-CL by focusing on the soft properties of molecular crystals (Hirano, Matsuhashi, et al.). Oxygenated anthracenes showing CL similar to those found in oxygenated rubrene (Fig. 3) were found, and crystal-specific reactivity and generation mechanisms of excited species were proposed (Hirano, Yamazaki, et al.).

4. Frontiers of reaction mechanism research

In the reaction mechanism, the chemiexcitation process that gives the product in the excited singlet state is important in the thermolysis of peroxides. This process was investigated in relation to efficient firefly BL. In the 1980s, a CIEEL mechanism involving intramolecular electron transfer was proposed, that was modified to a CTIL mechanism involving intramolecular charge transfer by theoretical calculations (Yamaguchi, et al.). The accumulation of experimental facts supporting this theoretical prediction is awaited.

References

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Future Perspectives and Directions

Issues to be resolved and realized within the next 10 years: Adjustment of CL reactivity and characteristics by AI prediction, Development of stimuli-responsivities to extend analytical performance, Reaction mechanism elucidation in an unexplored reaction field, Experimental establishment of chemiexcitation mechanisms.

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