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Mechanistic Aspects of Bioluminescence and Chemiluminescence

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Abstract: Bicyclic dioxetane bearing a (3-cyanoethenyl) phenyl group was found to be triggered by the Michael addition of a malonate anion with an accompanying emission of red light. 3-Adamantylidene-4-methoxy-1,2-dioxetanes bearing a 4-(3-hydroxy)phenyl substituted with a podand-type group, namely, 1,4,7-trioxaoctyl, 1,4,7,10-tetraoxaundecyl, or 1,4,7,10,13 -pentaoxa- tetradecyl were synthesized and their base-induced chemiluminescent decomposition was examined in an aqueous system. Optically active dioxetanes bearing a naphthyl naphthol moiety were also synthesized. They exhibited chemiluminescence in molecular recognition.

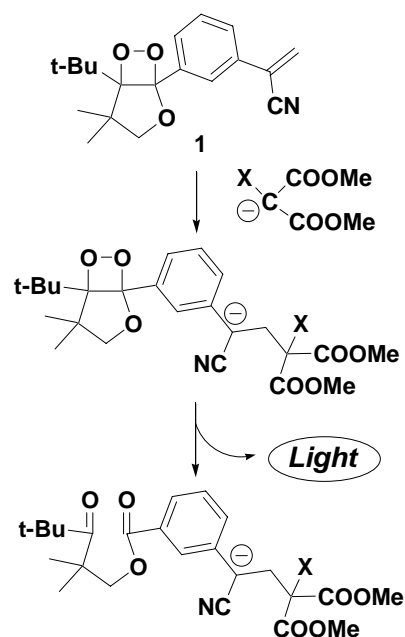
Keywords: dioxetane, chemiluminescence, Michael addition, molecular recognition

Introduction

High-energy molecules, 1,2-dioxetanones, are believed to participate as a precursor emitting light for bioluminescences of the firefly, and the jelly-fish *Aequorea Victoria*. However, the detail mechanistic aspects, especially singlet-chemiexcitation process, are yet remained as unfinished business to be investigated more and more. Our project is to solve such crucial problem from the viewpoint of design for highly efficient dioxetane-based chemiluminescent substrates.

Chemiluminescent decomposition of a dioxetane bearing a 3-(1-cyanoethenyl)- phenyl moiety induced by Michael addition of an anion of malonate⁹⁾

Thermally stable dioxetane bearing a 3-(1-cyanoethenyl) phenyl group (1) was synthesized. Michael addition of an anion of malonate to a dioxetane (1) took place to give an intermediary dioxetane bearing a benzylic anion, which decomposed rapidly with accompanying emission of crimson light. When an anion of chloromalonate was used as a base, intramolecular cyclopropanation of 1 occurred concurrently with the Michael addition induced chemiluminescent decomposition (Scheme 1).

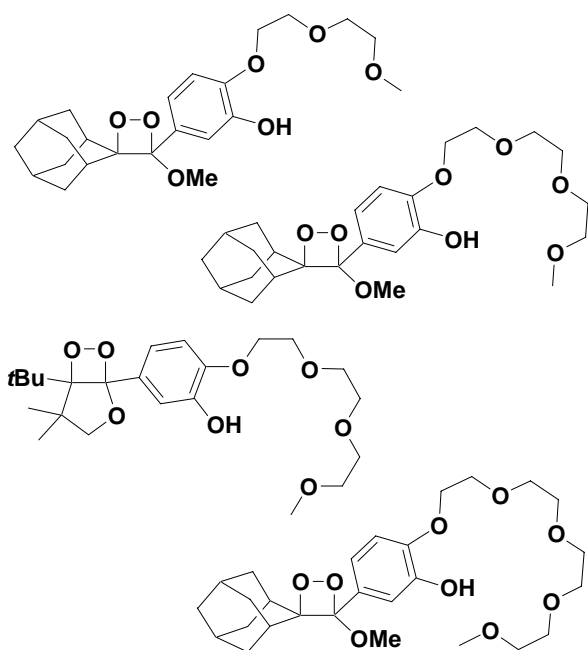


Scheme 1.

Electron-transfer-induced chemiluminescent decomposition of dioxetanes bearing a 3-hydroxyphenyl substituted with a podand-type group⁹⁾

3-Adamantylidene-4-methoxy-1,2-dioxetanes bearing a 4-(3-hydroxy)phenyl substituted with a podand-type group, namely, 1,4,7-trioxaoctyl, 1,4,7,10-tetraoxaundecyl, or 1,4,7,10,13-pen-

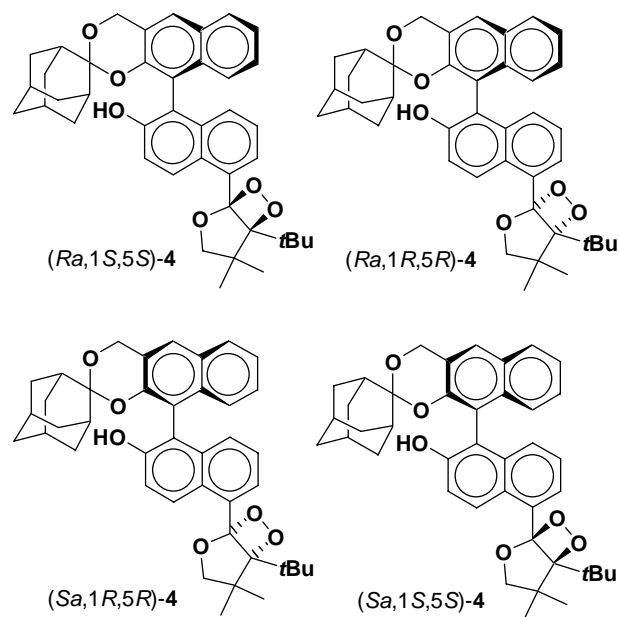
taoxatet - radeacyl were synthesized. A bicyclic dioxetane, 5-*t*-butyl - 4, 4-dimethyl-2, 6, 7-trioxabicyclo [3.2.0]heptane, bearing a 3-hydroxy-4-(2,5,8,11-tetraoxadodecyl)phenyl at the 1-position was also synthesized. On treatment with tetrabutylammonium fluoride in DMSO or acetonitrile, all these dioxetanes decomposed rapidly with accompanying emission of flash blue light. In NaOH / H₂O system, these dioxetanes decomposed also rapidly to emit light though the chemiluminescent efficiency was significantly decreased. However, the introduction of a podand-type substituent, namely, 2,5,8,11-tetraoxadodecyl was rather effective to improve both chemiluminescent efficiency and ET-induced decay-rate of dioxetane (Scheme 2).



Scheme 2.

Chemiluminescence in molecular recognition: base-induced decomposition of optically active dioxetanes bearing a bisnaphthol moiety with a complex of optically active crown ether / potassium *t*-butoxide⁹

Four optically pure isomers of dioxetane bearing a naphthyl-naphthol moiety decomposed by the action of complex of optically active crown ether with potassium *t*-butoxide to afford light with $\lambda_{\max}^{\text{CL}}$ and shape of spectrum different from each other (Scheme 3).



Scheme 3.

Advanced Chemistry of Dioxetane-Based Chemiluminescent Substrates Originating from Bioluminescence⁹

High-energy molecules, 1,2-dioxetanes, have received a great deal of attention because of their unique property to decompose thermally into electronically excited carbonyl products. Their chemistry originates from studies on molecular mechanisms of bioluminescence and has a history of over 30 years. However, the luminescent efficiency of the dioxetanes realized could hardly be compared with bioluminescence until a dioxetane bearing an aryl group oxidized easily was found to afford efficient chemiluminescence by the intramolecular CIEEL (chemically initiated electron exchange luminescence) mechanism. Nowadays, the CIEEL-type dioxetanes are being applied to the modern biochemical and biomedical analyses. In this review, the advanced chemistry of the CIEEL-type dioxetanes as a highly efficient chemiluminescent substrate is described focusing on their molecular design and synthesis. Singlet chemiexcitation processes for the intramolecular CIEEL-decay of dioxetanes and triplet-chemiexcitation processes for thermolysis of dioxetanes are also discussed.

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