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Recognition of Metal Ions by Chemiluminescence using 2-(*N*,*N*-Dimethylamino) Tryptanthrin and *N*-(2-(2,2'-Dipicolylamino)Ethyl)Aniline

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Abstract

We investigated metal ion recognition using peroxyoxalate chemiluminescence (POCL) in acetonitrile. The fluorescent dye 2-(*N*,*N*-dimethylamino)tryptanthrin (**T2NMe$_2$**) and the metal ion ligand *N*-(2-(2,2'-dipicolylamino)ethyl)aniline (**DPEA**) were used. In the absence of metal ions, fluorescence was not observed due to intermolecular electron transfer from **DPEA** to 1,2-dioxetanedione of the reaction intermediate. However, the ionization potential of the **DPEA**-metal complexes formed when **DPEA** coordinated with metal ions increased in their presence. This enabled chemiluminescent fluorescence via intermolecular electron transfer, also known as chemically initiated electron exchange luminescence (CIEEL), between **T2NMe$_2$** and 1,2-dioxetanedione. The order of selectivity toward metal ions based on fluorescence intensity was as follows: $Pb^{2+} \gg Cu^{2+} > Zn^{2+} > Ag^{+} \gg Li^{+} > Cd^{2+} > Ba^{2+} \approx Mg^{2+}$.

Key-words: *Chemiluminescence, Metal ion, Chemically initiated electron exchange luminescence, Tryptanthrin*

1. Introduction

Fluorescent analytical reagents, including chemosensors and probes based on organic fluorescent dyes, are simple yet highly versatile. These reagents are particularly indispensable for studying biological phenomena in the life sciences[1,2]. Fluorescent analytical reagents consist of a recognition site for target molecules or ions and a fluorescent dye site. However, some fluorescent dyes require ultraviolet light irradiation to be excited, and this cannot be used in living organisms due to concerns about cell damage. In this study, therefore, we investigated the use of chemiluminescence, which generates an excited state through a chemical reaction without requiring excitation light. 2-(*N*,*N*-dimethylamino) tryptanthrin (**T2NMe$_2$**)[3] was used as the fluorescent dye and *N*-(2-(2,2′-dipicolylamino)ethyl)aniline (**DPEA**)[4] as the metal ion ligand (**Fig. 1**). Chemiluminescence was performed using peroxyoxalate chemiluminescence (POCL)[5] as shown in **Fig. 2**. In POCL, the reaction intermediate,

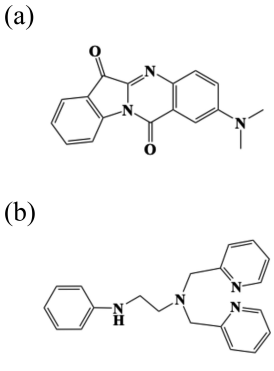

Fig. 1 Structural formulas of (a) **T2NMe$_2$** and (b) **DPEA**.

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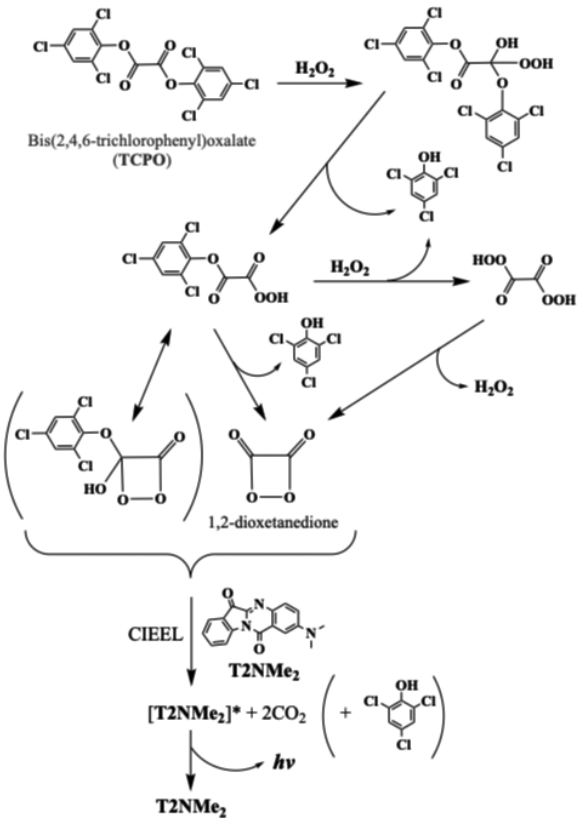

Fig. 2 Reaction mechanism of POCL.