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Hydrogen bonding network-assisted chemiluminescent thermal decomposition of 3-hydroxyphenyl-substituted dioxetanes in crystal

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A B S T R A C T

Bicyclic dioxetane **1** bearing a 3-hydroxyphenyl group underwent thermal decomposition in solution (TD_{soln}) to form 3-oxopentyl 3-hydroxybenzoate **4** accompanied by the emission of light [$\lambda_{\max}^{CL}$ (TD_{soln}) = 405 nm] due to an excited 3-oxopentyl group in **4**. Dioxetane **1** also exclusively gave **4** by thermal decomposition in crystal (TD_{cryst}). However, in contrast to TD_{soln}, TD_{cryst} of **1** gave light [$\lambda_{\max}^{CL}$ (TD_{cryst}) = 464 nm] due to excited oxidobenzoate **3*** and/or its closely related species formed by CTID (charge-transfer induced decomposition) mechanism. The unique chemiluminescent TD_{cryst} of **1** was presumably the result of hydrogen bonding formed in the crystal between the phenolic proton of a dioxetane molecule and a peroxide oxygen of another dioxetane molecule. In this work, TD_{cryst} as well as TD_{soln} of bicyclic dioxetane analog bearing a 4-fluorenyl-3-hydroxyphenyl moiety **10** and of adamantylidene-dioxetane bearing a 3-hydroxyphenyl group **5b** were also investigated.

Deprotonation of a 3-hydroxyphenyl-substituted bicyclic dioxetane **1** with a base produces unstable dioxetane **2** bearing a phenoxide anion, which decomposes by intramolecular charge-transfer-induced decomposition (CTID) mechanism to effectively give 3-oxopentyl 3-oxidobenzoate **3** with the emission of bright blue light (Base-Induced Decomposition: BID) (Scheme 1).[1,2] On the other hand, when simply heated in a nonpolar solvent, dioxetane **1** decomposes to give 3-oxopentyl 3-hydroxybenzoate **4** accompanied by the emission of very weak light (Thermal Decomposition: TD). A similar tendency has been observed for an adamantylidene-substituted dioxetane **5a**, the BID of which effectively produces excited methyl 3-oxidobenzoate **6*** which emits blue light, while simple TD in solution gives light due to excited adamantanone **7***.[3] We report here that, in contrast to TD in solution (TD_{soln}), the TD of dioxetane **1** in crystal (TD_{cryst}) proceeded by CTID mechanism to give blue light due to excited 3-oxidobenzoate **3*** and/or its closely related species, rather than to an excited ketone moiety or an excited 3-hydroxybenzoate moiety in **4**.

When crystalline dioxetane **1** (mp 119.0 °C) was heated at 100 °C, the crystals of **1** emitted blue light, the spectrum of which had a maximum wavelength at $\lambda_{\max}^{CL}$ (TD_{cryst}) = 464 nm, as shown in Figure 1[(A)-(a)] and Table 1. On the other hand, TD_{soln} of **1** in hot *p*-xylene (110 °C) gave weak chemiluminescence with $\lambda_{\max}^{CL}$ (TD_{soln}) = 405 nm [Fig. 1(A)-(b), Table 1]. These results showed that the chemiluminescence for TD_{cryst} of **1** occurs via a mechanism different from that in the case of simple TD_{soln} in non-polar solvent (Scheme 1). Notably, ^{1}H NMR analysis showed that the spent crystalline mixture for TD_{cryst} exclusively gave keto ester **4** as in the case for TD_{soln}.

Thus, we measured the fluorescence of authentic keto ester **4** in crystal as well as in *p*-xylene solution. As shown in Figure 1[(B)-(a) and (b)] and Table 1, maximum wavelength of fluorescence, $\lambda_{\max}^{fl}$ (*soln*), was observed at 360 nm in *p*-xylene, while $\lambda_{\max}^{fl}$ (*cryst*) was observed at 346 nm in crystal. Next, we examined fluorescence of two model compounds in *p*-xylene**.** Methyl 3-hydroxybenzoate (**8**: Y = H) as a model of a 3-hydroxybenzoate moiety in **4** showed fluorescence with $\lambda_{\max}^{fl}$ (*soln*) = 344 nm, while di-*tert*-butyl ketone as a model of the ketone moiety in **4** showed fluorescence with $\lambda_{\max}^{fl}$ (*soln*) = 407 nm [Fig. 1(B)-(d) and (e)]. These results revealed that the chemiluminescence for TD_{soln} of **1** in *p*-xylene was undoubtedly due to an excited ketone moiety in **4**, while the chemiluminescence for TD_{cryst} of **1** could not be attributed to either the excited ketone moiety or the excited hydroxybenzoate moiety in **4**.

As has been reported for BID of **1**, intermediary oxidophenyl-substituted dioxetane **2** undergoes CTID to display chemiluminescence with $\lambda_{\max}^{CL}$ (BID) = 466–470 nm.[2] Figure 1(A) shows the chemiluminescence spectrum for BID of **1** in TBAF (tetrabutylammonium fluoride)/acetonitrile as a representative together with those for TD_{soln} and TD_{cryst} of **1**. A comparison of these spectra shows that the chemiluminescence spectrum for TD_{cryst} overlapped

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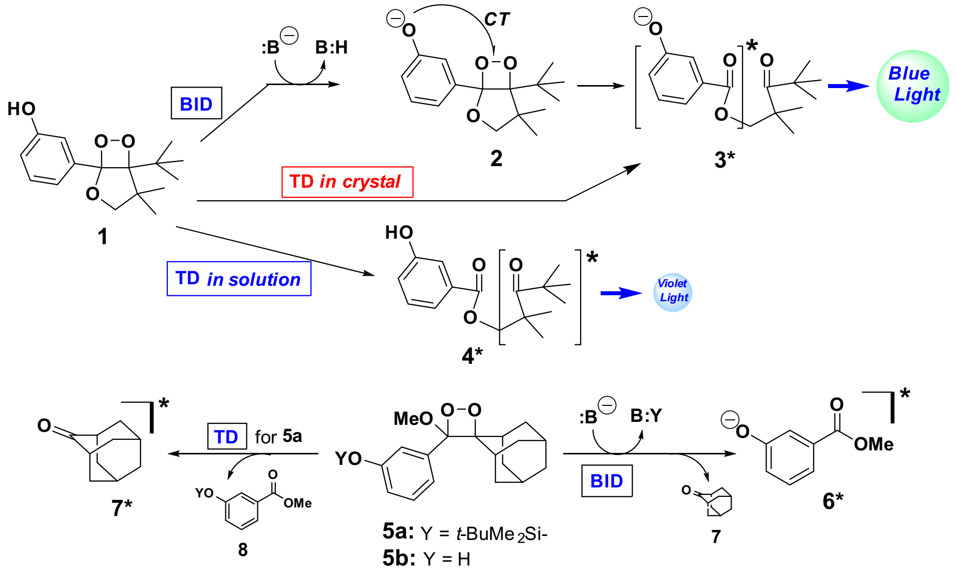

Scheme 1. Chemiluminescent decomposition of 3-oxyphenyl-substituted dioxetanes **1** and **5**.

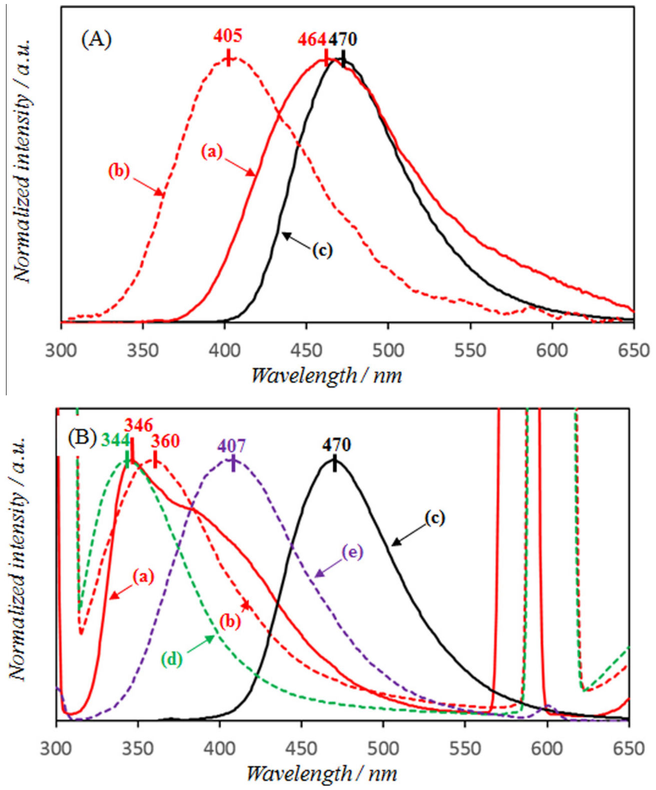

Figure 1. Chemiluminescence spectra of dioxetane **1** (A): (a) for TD$_{cryst}$, (b) for TD$_{soln}$ in *p*-xylene and (c) for BID in TBAF/acetonitrile. Fluorescence spectra (B): for ketoester **4** (a) in crystal, (b) in *p*-xylene and (c) in TBAF/acetonitrile, and (d) for methyl 3-hydroxybenzoate **8** in *p*-xylene and (e) for di-*tert*-butyl ketone in *p*-xylene.

Table 1
Maximum wavelength for chemiluminescence of dioxetanes **1**, **10** and **5b** and maximum wavelength for fluorescence of ketoesters **4** and **12**

λ^{CL}_{max} for chemiluminescence of dioxetane/nm				λ^{fl}_{max} for fluorescence of authentic emitter/nm			
	BID[a]	TD$_{soln}$[b]	TD$_{cryst}$[c]		Basic soln[a]	Neutral soln[d]	Crystal[e]
1	470	405	464	**4**	470	360, 407[f]	346
10	500	377	398	**12**	500	381	388
5b	469	428	451	**8**[g]	470	344, 430[h]	–

[a] 25 °C in TBAF/acetonitrile.
[b] 110 °C in *p*-xylene.
[c] 100 °C.
[d] 25 °C in *p*-xylene.
[e] 25 °C.
[f] Di-*tert*-butyl ketone.
[g] Y = H.
[h] Adamantanone **7**.

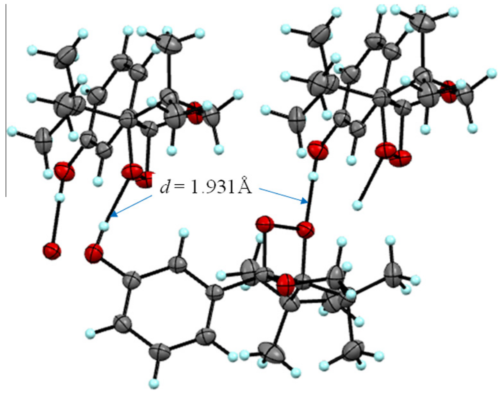

Figure 2. View of the intermolecular hydrogen bonding network for dioxetane **1** in crystal.

that for BID, though the former somewhat broadened, especially in the shorter wavelength region. Thus, the TD$_{cryst}$ of **1** was presumed to proceed by a CTID mechanism as in the case of BID.

To better understand the significant difference in the chemiluminescence of **1** between TD$_{soln}$ and TD$_{cryst}$, we performed an X-ray single crystallographic analysis of **1**.[4,5] As shown in Figure 2, dioxetane **1** in crystal formed a network constructed by intermolecular hydrogen bonding between a phenolic OH of one molecule and a peroxide oxygen of another molecule (bond length d = 1.931 Å and bond angle θ = 173.7°).[6] Thus we can imagine that,