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NOTABLE DIFFERENCE BETWEEN TETRABUTYLAMMONIUM FLUORIDE AND ORGANIC SUPERBASES AS TRIGGERS FOR THE CHEMILUMINESCENT DECOMPOSITION OF BICYCLIC DIOXETANES BEARING A 4-(*N*-PHENYLBENZIMIDAZOL-2-YL)-3-HYDROXYPHENYL MOIETY

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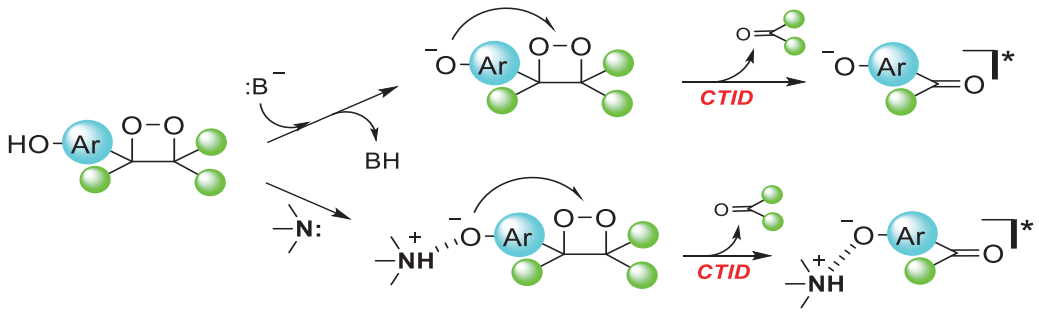
Abstract – Chemiluminescent decomposition of bicyclic dioxetanes **3a**−**3c** bearing a 4-(*N*-phenylbenzimidazol-2-yl)-3-hydroxyphenyl moiety was effectively induced by organic superbases, BTPP [(*tert*-butylimino)tris-(pyrrolidino)phosphorene], TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene), DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene), and TMG (tetramethylguanidine), as well as TBAF in acetonitrile. Dioxetane **3c** bearing a 3,5-dihydroxyphenyl moiety showed diverse chemiluminescence profiles depending on the base used. BTPP caused chemiluminescent decomposition due to the di-oxido anion of dioxetane, while DBU and TMG induced chemiluminescence from the mono-oxido anion of dioxetane. On the other hand, TBAF caused effective chemiluminescence due to the mono-oxido anion, though it acted as a stronger base than BTPP with regard to the rate of decomposition of **3c**.

INTRODUCTION

Deprotonation of a dioxetane bearing a hydroxyaryl group with a base produces an unstable oxidophenyl-substituted dioxetane, which undergoes intramolecular charge-transfer-induced decomposition (CTID) to generate a singlet-excited oxidoaryl-substituted carbonyl fragment while

effectively emitting light (Scheme 1).[1-7] For the base-induced decomposition (BID) of dioxetanes, inorganic ionic bases such as F^- and OH^- have generally been used, while organic neutral bases have been used relatively little, presumably because of their possible nucleophilic attack of O-O and catalysis of the radiationless decomposition of dioxetane.[8,9] We have very recently found that a) organic superbases induce the chemiluminescent decomposition of parent bicyclic dioxetane **1** and its derivatives bearing a 4-(benzoxazol-2-yl)-3-hydroxyphenyl moiety **2a**–**2c** (Figure 1) as effectively as, or more effectively than, TBAF (tetrabutylammonium fluoride), b) the color of the chemiluminescence from dioxetane **2c** bearing a 4-(benzoxazol-2-yl)-3,5-dihydroxyphenyl moiety changes depending on the base used, and c) in addition to this difference in the color of emission, the bifunctional superbase TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) has a unique effect on the chemiluminescent decomposition of **2c**: TBD markedly increases the chemiluminescence efficiency compared to with other bases and accelerates decomposition of the dioxetane.[10]



Scheme 1. Base-induced chemiluminescent decomposition of a hydroxyaryl-substituted dioxetane

These characteristic features of the chemiluminescent decomposition of **2a**–**2c** with the use of organic superbases were apparently due to the formation of a contact ion-pair between a conjugate acid of a superbase and an oxidophenyl-substituted dioxetane (Scheme 1). Thus, we decided to further investigate the superbase-induced decomposition of dioxetanes **3a**–**3c** which possessed a sterically-congested *N*-phenylbenzimidazol-2-yl moiety instead of a benzoxazole moiety as in **2a**–**2c** (Figure 1).

Dioxetane **3a** bearing a 4-(*N*-phenylbenzimidazol-2-yl)-3-hydroxyphenyl moiety has been reported to be one of the most effective CTID-active dioxetanes,[11] while **3c** bearing a 4-(*N*-phenylbenzimidazol-2-yl)-3,5-dihydroxyphenyl moiety was designed to compare its chemiluminescence profiles to those of benzoxazole-analog **2c**, which decomposed through mono-oxido anion, di-oxido anion, or contact ion-pair complex(es). We selected as a trigger five typical superbases, BTPP [(*tert*-butylimino)tris-(pyrrolidino)phosphorene], TBD, MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and TMG (tetramethylguanidine), together with TBAF

(tetrabutylammonium fluoride) as a reference (Figure 1): ^{AN}pKa (p*K*a in acetonitrile) = 28.4 for BTPP, 26.0 for TBD, 25.5 for MTBD, 24.3 for DBU, and 23.4 for TMG.[12]

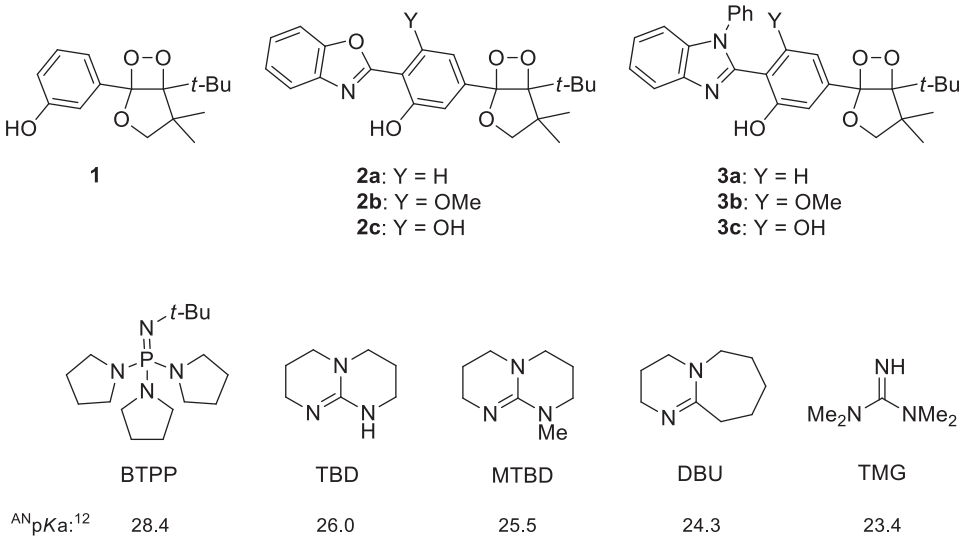


Figure 1. Bicyclic dioxetanes bearing a hydroxyaryl moiety and organic-superbases

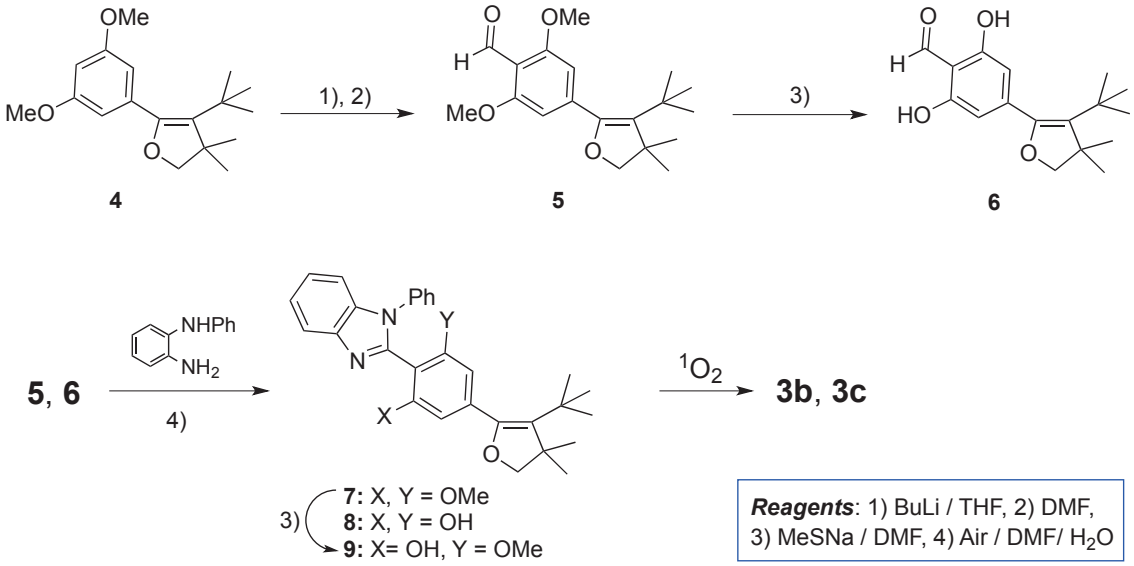
We found that a) organic superbases effectively acted as triggers for the chemiluminescent decomposition of dioxetanes **3a** and **3b** as well as **2a** and **2b** in acetonitrile, b) similarly to **2c**, **3c** showed diverse chemiluminescence profiles depending on the superbase used, and c) the formation of a contact ion-pair between a conjugate acid of a superbase and an oxidophenyl-substituted dioxetane was suggested to play an important role in the CTID of **3a**−**3c**, as in the case of **2a**−**2c**. In addition to these findings, we report that TBAF showed a notable difference from organic superbases as a trigger for BID of **3c**: TBAF behaved as the strongest base among those used for **2c**, while it caused emission of bright light from a mono-oxido anion form of **3c**, as with weaker bases such as DBU and TMG, though it was a stronger base than BTPP with regard to the rate of decomposition.

RESULTS AND DISCUSSION

Synthesis of bicyclic dioxetanes bearing a 4-(*N*-phenylbenzimidazol-2-yl)-3-hydroxyphenyl moiety

The synthesis of dioxetanes **3b** and **3c** will be described here; that of **3a** has been reported previously.[11] These dioxetanes were prepared by singlet oxygenation of the corresponding 2,3-dihydrofurans **8** and **9** bearing a 4-(*N*-phenylbenzimidazol-2-yl)-3-hydroxyphenyl moiety at the 5-position (Scheme 2). Synthesis of the precursors **8** and **9** started from 5-(3,5-dimethoxyphenyl)dihydrofuran **4**. The lithiation of **4** with BuLi followed by the addition of DMF gave benzaldehyde **5**, the demethylation of which smoothly took place with MeSNa in hot DMF to give 3,5-dihydroxybenzaldehyde **6**. When benzaldehydes **5** and **6** were individually treated with *N*-phenyl-*o*-phenylenediamine in wet DMF under

aerobic conditions, the corresponding *N*-phenylbenzimidazolylphenyl-substituted dihydrofurans **7** and **8** were effectively produced. Demethylation of **7** was effectively attained by the use of MeSNa in hot DMF to give **9**. Dihydrofurans **8** and **9** underwent sensitized photooxygenation in AcOEt at 0 °C to selectively give the corresponding dioxetanes **3c** and **3b**. These dioxetanes **3b** and **3c** were thermally stable to permit handling at room temperature, but decomposed to selectively give the corresponding keto esters **10b** and **10c** in refluxing *p*-xylene (Scheme 3).



Scheme 2. Synthesis of bicyclic dioxetanes bearing a hydroxyaryl moiety

Chemiluminescent decomposition of bicyclic dioxetanes bearing a 4-(*N*-phenylbenzazimidazol-2-yl)-3-hydroxyphenyl moiety

When **3a** (3.3 x 10^{-5} M) was treated with a large excess (200 eq.) of BTPP in acetonitrile at 45 °C, **3a** decomposed according to pseudo-first order kinetics to give bright blue light (maximum wavelength: λ_{max}^{CL} = 492 nm, rate constant of CTID: k^{CTID} = 3.2 x 10^{-2} s^{-1}, half-life of CTID: $t_{1/2}$ = 22 s, and chemiluminescence efficiency Φ^{CL} = 0.20).[13,14] If we compare these results to those for **3a** in a TBAF system (λ_{max}^{CL} = 492 nm, k^{CTID} = 2.6 x 10^{-2} s^{-1}, $t_{1/2}$ = 27 s, and Φ^{CL} = 0.22), we can see that BTPP was as effective as TBAF. Chemiluminescent decomposition of **3a** was similarly carried out with TBD, MTBD, DBU and TMG. The results are summarized in Table 1 and Figure 2(A), which shows that **3a** displayed chemiluminescence with λ_{max}^{CL} = 492 nm and a high Φ^{CL} (0.20−0.24) regardless of the base used, and k^{CTID} decreased in the order of the strength of the bases, BTPP > MTBD > DBU > TMG, except for TBD: k^{CTID} for TBD was smaller than that for MTBD, though TBD was a stronger base than MTBD. A similar tendency was observed for the chemiluminescent decomposition of dioxetane **3b**, as shown in Table 1 and Figure 2(C). These results are illustrated together with those for benzoxazole analogs **2a**−**2b**[10] in Figure 3. As shown in Figure 3, the chemiluminescence profiles of *N*-phenylbenzimidazole

analogs **3a** and **3b** quite resembled those of benzoxazolylphenol-substituted dioxetanes **2a** and **2b** with the use of organic superbases and TBAF. We should note here that a) for all of the base systems, a freshly spent reaction mixture of **3a** and **3b** selectively gave the corresponding keto esters **10a** and **10b** after careful neutralization, and b) authentic oxido-anions **12a** and **12b** prepared by individually dissolving **10a** and **10b** in base/acetonitrile showed intense fluorescence, the spectra of which practically coincided with the respective chemiluminescence spectra of **3a** and **3b** [Figure 2 (B), (D)]. Thus, we know that the base-induced decomposition of **3a** and **3b** proceeded through an oxido anion form of dioxetane **11a** and **11b** to give excited **12a** and **12b**, respectively (Scheme 3).

Table 1. Chemiluminescence properties for organic superbase-induced decomposition of dioxetanes **3a**−**3c** in MeCN[a)]

	Base	BTPP	TBD	MTBD	DBU	TMG	TBAF
	^{AN}pKa[b)]	28.4	26	25.5	24.3	23.4	-----
3a	λ_{max} /nm	492	492	492	492	492	492
	Φ^{CL}	0.20	0.22	0.24	0.22	0.22	0.22
	k^{CTID}/ s^{-1}	3.2×10^{-2}	6.4×10^{-3}	9.8×10^{-3}	3.2×10^{-3}	7.8×10^{-4}	2.6×10^{-2}
	$t_{1/2}$/ s	22	110	71	220	890	27
3b	λ_{max} /nm	480	480	480	480	480	480
	Φ^{CL}	0.23	0.23	0.23	0.21	0.22	0.19
	k^{CTID}/ s^{-1}	1.6×10^{-2}	3.3×10^{-3}	7.1×10^{-3}	5.3×10^{-3}	3.6×10^{-3}	1.6×10^{-2}
	$t_{1/2}$/ s	43	210	98	130	190	43
3c (25°C)	λ_{max} /nm	532	520	518	498	498	501
	Φ^{CL}	4.9×10^{-4}	6.5×10^{-3}	5.9×10^{-3}	9.6×10^{-3}	1.3×10^{-2}	8.8×10^{-3}
	k^{CTID} / s^{-1}	1.5	3.6	7.9×10^{-2}	9.8×10^{-3}	5.5×10^{-3}	16
	$t_{1/2}$ / s	0.46	0.19	8.8	71	150	0.04

a) Unless otherwise stated, a solution of a dioxetane in MeCN (1.0×10^{-4} M, 1 mL) was added to a solution of a base in MeCN (1.0×10^{-2} M, 2 mL) at 45 °C. b) Ref. 12.

Next, we investigated the chemiluminescent BID of dioxetane **3c** bearing a 3,5-dihydroxyphenyl moiety. When treated with a large excess (200 eq.) of BTPP at 25 °C in acetonitrile, **3c** decomposed to emit a flash of yellowish green light (λ_{max}^{CL} = 532 nm, $t_{1/2}$ = 0.46 s, and $\Phi^{CL} = 4.9\times10^{-4}$). On the other hand, upon treatment with a weaker base such as DBU or TMG, **3c** gave a glowing greenish blue light (λ_{max}^{CL} = 498 nm), though the Φ^{CL} values were far higher than in the case of BTPP: $t_{1/2}$ = 71 s, $\Phi^{CL} = 9.6\times10^{-3}$ for DBU; $t_{1/2}$ = 150 s, $\Phi^{CL} = 1.3\times10^{-2}$ for TMG (Table 1, Figure 2(E), and Figure 3). Regarding the

chemiluminescence seen with **3a** and **3b**, the emission from **3c** in the DBU or TMG system was

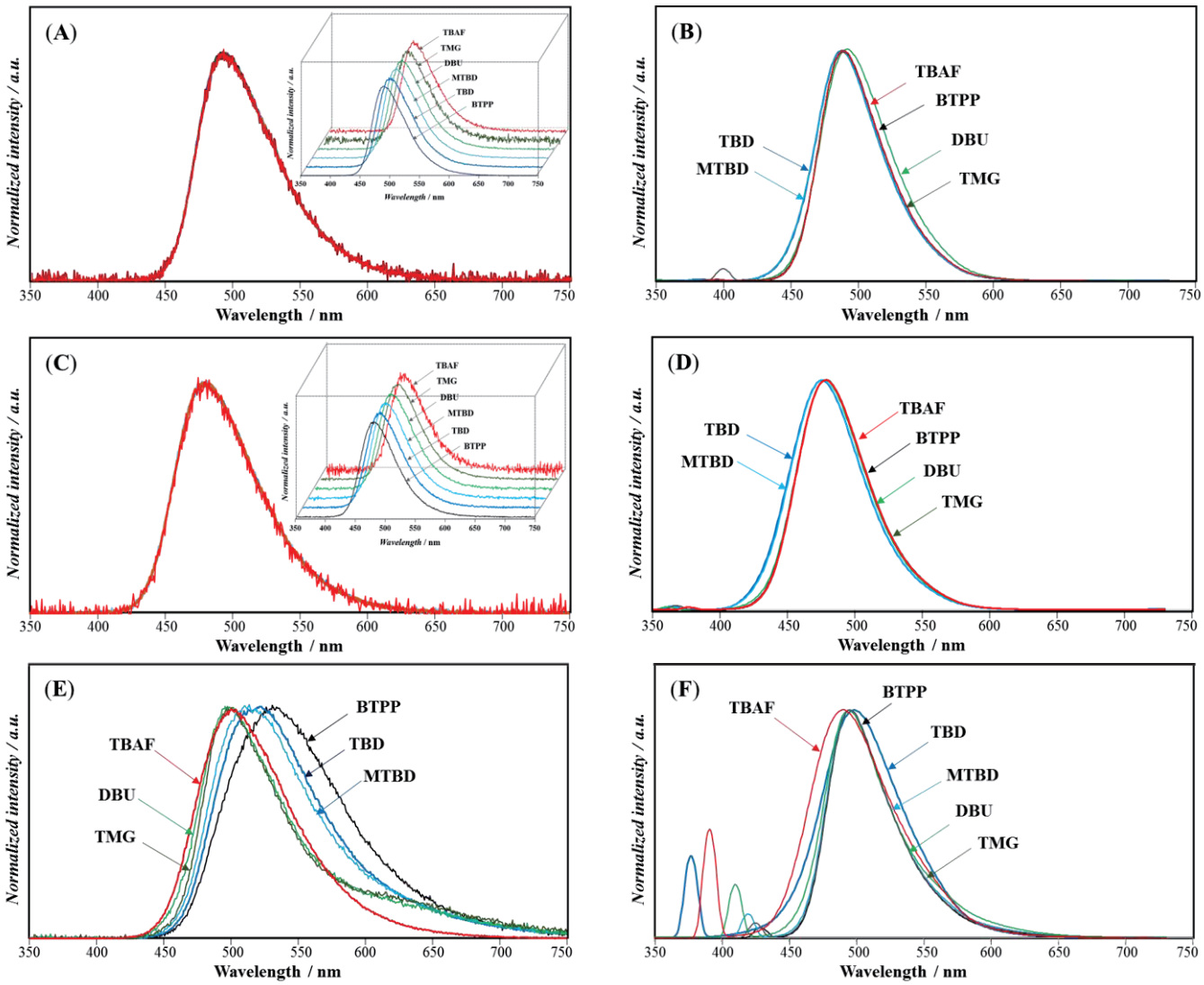
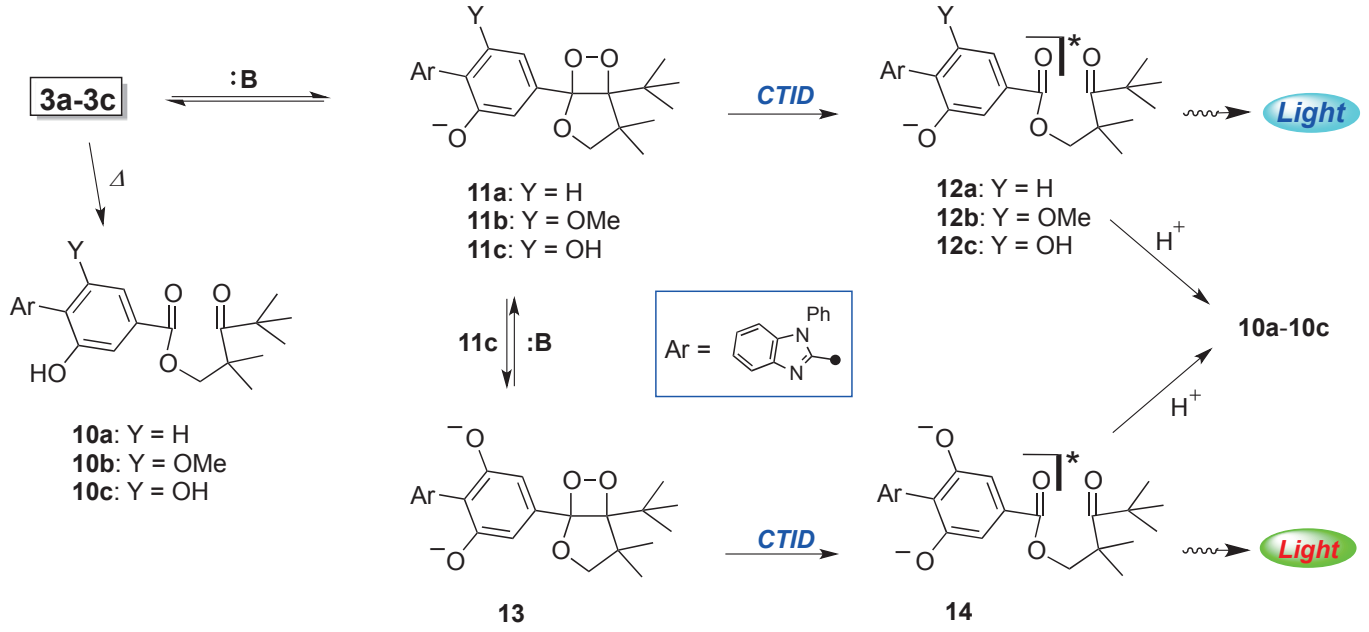


Figure 2. Chemiluminescence spectra of (A) dioxetane **3a**, (C) **3b**, and (E) **3c**, and fluorescence spectra of (B) **10a** and (D) **10b**, and (F) **10c** in a base/MeCN system

undoubtedly due to CTID of the mono-oxido anion form **11c** of dioxetane, which gave excited oxidobenzoate **12c** (Scheme 3): authentic **10c** showed fluorescence with maximum wavelength λ_{max}^{fl} = 495 nm in DBU or TMG / acetonitrile [Figure 2 (F)] Thus, on further reflection, BTPP (large excess) presumably induced the decomposition of **3c** through the di-oxido anion form **13** of dioxetane, which rapidly decomposed to excited dioxidobenzoate **14**, as shown in Scheme 3.[15]

When treated with TBD (200 eq.), **3c** decomposed even faster than with the stronger base BTPP to emit a bluish green light: the λ_{max}^{CL} (= 520 nm) was 12 nm shorter than that in the BTPP system but ca. 20 nm longer than those in the DBU and TMG systems (Figure 2). Notably, Φ^{CL} of **3c** in the TBD system was

>10-fold greater than that in the BTPP system. Treatment with MTBD caused chemiluminescent decomposition of **3c** to also give greenish blue light (λ_{max}^{CL} = 518 nm), though it did not accelerate the rate of CTID. These results are summarized in Table 1 and illustrated in Figure 3, from which we know that TBD had a unique effect, distinct from those of the other superbases, on the chemiluminescence profiles in the BID of **3c**.



Scheme 3. Thermal decomposition and base-induced chemiluminescent decomposition of bicyclic dioxetanes bearing a hydroxyaryl moiety

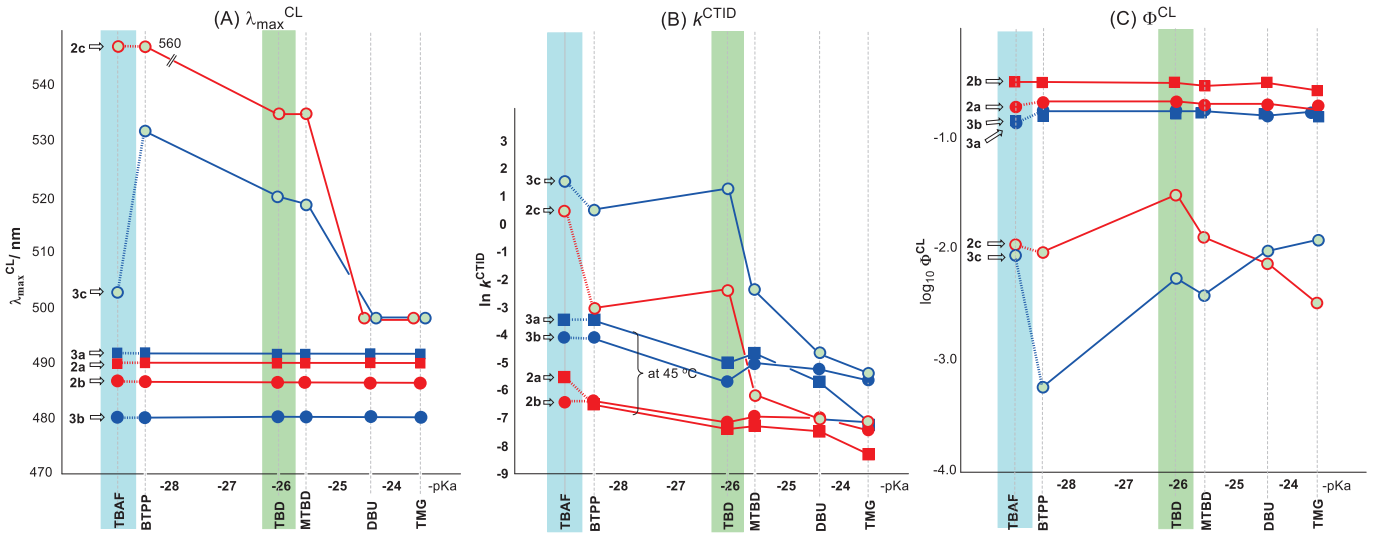
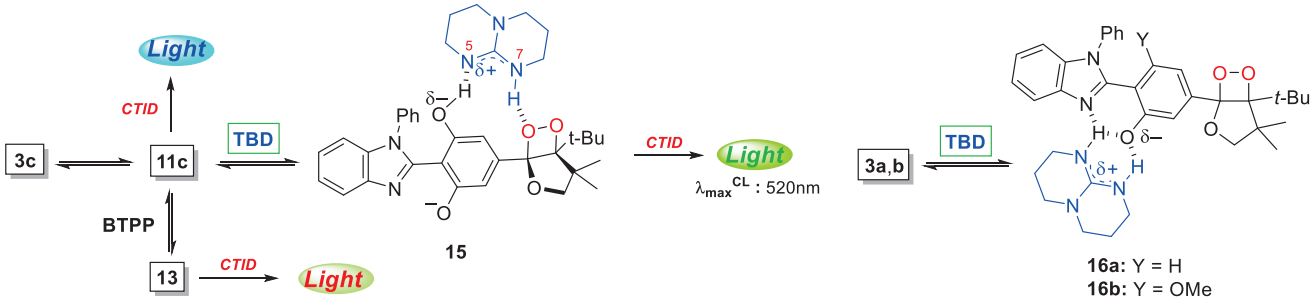


Figure 3. Relationships of the strength of superbases to (A) λ_{max}^{CL}, (B) k^{CTID}, and (C) Φ^{CL} for the base-induced decomposition of bicyclic dioxetanes bearing a hydroxyaryl moiety in MeCN

As has been previously reported for **2c**,[10] the diverse chemiluminescence profiles of **3c** in the superbase systems can be explained as follows. The first dissociation of two phenolic OH groups in **3c** easily occurs to give mono-oxido anion **11c**, while dissociation of the remaining phenolic OH of **11c** would become far harder. Therefore, **11c** decomposes without the formation of di-oxido anion **13** in a weaker base (DBU or TMG) system, while **11c** forms **13** in a stronger base (BTPP) system. TBD and MTBD are not strongly basic enough to produce **13**, but could participate in CTID of **3c**, presumably through the formation of a contact ion-pair or polarized hydrogen bonding with a 5-hydroxy group of the initially formed **11c**. We notice here that TBD is a bifunctional guanidine base, distinct from the other superbases.[16] Thus, conjugate acid $TBDH^+$, as soon as it is formed by accepting a proton at N_5, can act as a proton donor at N_7, especially when it forms a contact ion-pair. Based on this idea, a second TBD molecule would react at N_5 with 5-OH of **11c** to form a contact ion-pair (or polarized hydrogen bond) and at the same time form a hydrogen bond between its N_7H and dioxetane O-O. Thus, a contact ion-pair complex as in **15** is presumably formed in the TBD system (Scheme 4). Protonation to dioxetane O-O through hydrogen bonding would accelerate the decomposition of dioxetane, as suggested previously.[17] Coordination of a second TBD molecule would prevent the aromatic ring from rotating around the axis joining it to the dioxetane ring in complex **15**. As illustrated in Scheme 4, 3-oxidophenyl of **15** lays in an *anti*-conformation so that singlet-chemiexcitation from **15** may occur more effectively than in the case where 3-oxidophenyl freely rotates, according to recent reports on the relationship of Φ^{CL} to the *syn*/*anti* rotational isomerism of an aromatic electron donor for CTID of bicyclic dioxetanes related to **1**.[18,19] Finally, we should suggest that TBD may favorably form a contact ion-pair even in the first dissociation of two phenolic OH of **3c** giving **11c**. This notion can presumably also apply to the dissociation of **3a** and **3b**, where mono-oxido anions **11a** and **11b** form respective contact ion-pairs, as in **16** (Scheme 4).[20]



Scheme 4. Formation of a contact ion-pair for the TBD-induced chemiluminescent decomposition of **3**

As described already, the BID of **3c** with the use of BTPP (large excess) proceeded through di-oxido anion **13** of dioxetane. For **2c**, in addition to BTPP, TBAF also caused chemiluminescence through the corresponding di-oxido anion of dioxetane to emit a flash of yellow light.[10] Furthermore, TBAF acted

as effectively as BTPP for BID of both **3a**, **3b** and **2a**, **2b** (Table 1 and Figure 3).[10] However, TBAF, as a trigger for the decomposition of **3c**, gave results that were notably different from those expected based on the results with **3c** in BTPP or **2c** in TBAF or BTPP. Upon treatment with TBAF (200 eq.) at 25 °C, **3c** decomposed more rapidly than with the other superbases investigated here to give a flash of greenish blue light, the λ_{max}^{CL} of which practically coincided with that of a glowing greenish blue light from mono-oxido anion **12c** as observed in a DBU or TMG system (Table 1 and Figure 3). On the other hand, Φ^{CL} for **3c** was ca. 20-fold higher with TBAF than with BTPP and comparable to that with TMG. Conclusively, TBAF caused effective emission of blue light from mono-oxido anion **12c**, similar to the weaker bases such as DBU and TMG, but acted as a base stronger than BTPP with regard to the rate of decomposition of **3c**.

Next, we investigated how the chemiluminescence profiles of **3c** changed with the concentration of BTPP or TBAF in acetonitrile. Upon treatment with 3.3 x 10^{-4} M (10 eq.) of BTPP, **3c** (3.3 x 10^{-5} M) emitted greenish blue light with λ_{max}^{CL} = 501 nm due to CTID of mono-oxido anion **11c**, though $t_{1/2}$ was far shorter, and Φ^{CL} was far lower, than in the DBU system, which caused effective chemiluminescence from **11c** (Table 1 and Table 2). When 20 eq. of BTPP was used, **3c** decomposed 10 times more rapidly but gave light with only 1/3 of Φ^{CL}, compared to the case with 10 eq. of BTPP. Notably, the chemiluminescence spectrum (λ_{max}^{CL} = 507 nm) of **3c** in 20 eq. of BTPP well-coincided with a spectrum that reflected 25% of that (λ_{max}^{CL} = 532 nm) in 200 eq. of BTPP and 75% of that (λ_{max}^{CL} = 501 nm) in 10 eq. of BTPP: the result suggested that merged chemiluminescence was observed from **12c** (25%) and **11c** (75%).

Table 2. Concentration effect of BTPP or TBAF on chemiluminescent BID of dioxetane **3c** in MeCN[a)]

Base	BTPP				TBAF			
equivalent	200	20	10	2	200	20	10	2
λ_{max} /nm	532	507	501	501	501	501	501	501
Φ^{CL}	4.9×10^{-4}	4.9×10^{-4}	1.7×10^{-3}	1.2×10^{-3}	8.8×10^{-2}	1.2×10^{-2}	1.5×10^{-2}	1.2×10^{-2}
k^{CTID}/ s^{-1}	1.5	1.5×10^{-1}	5.6×10^{-2}	-----	16	4.6×10^{-2}	9.9×10^{-3}	-----
$t_{1/2}$/ s	0.46	4.6	12	83	0.04	15	70	160

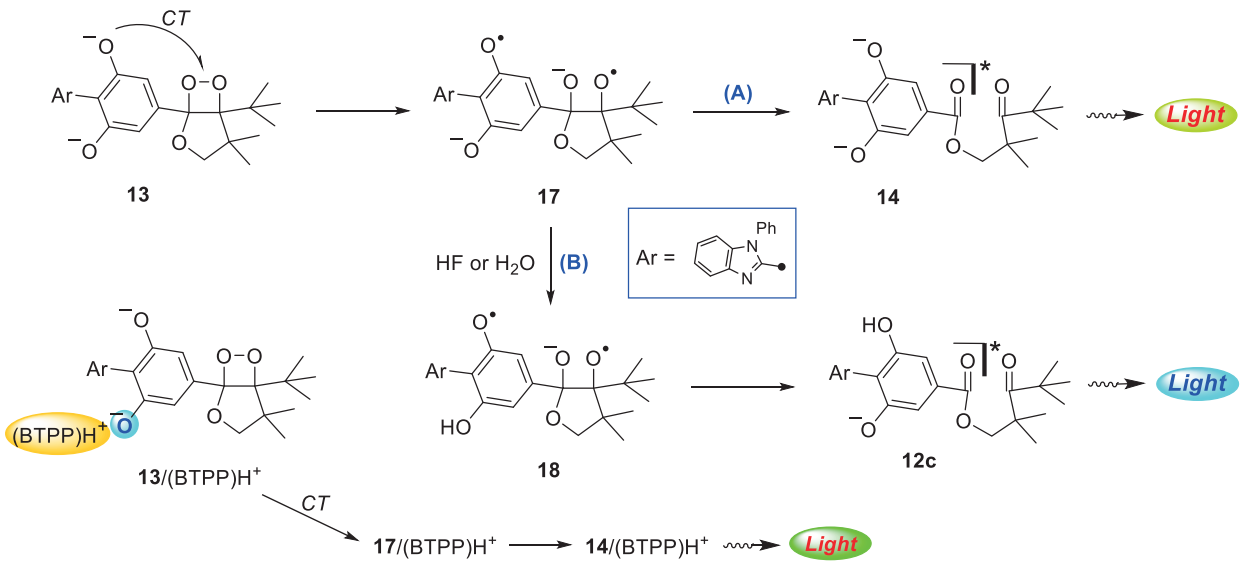
a) A solution of dioxetane **3c** in MeCN (1.0 x 10^{-4} M, 1 mL) was added to a solution of a base in MeCN (1.0 x 10^{-2}, 1.0 x 10^{-3}, 5.0 x 10^{-4}, or 1.0 x 10^{-4} M, 2 mL) at 25 °C.

On the other hand, as summarized in Table 2, the chemiluminescence profiles of **3c** in 2~200 eq. of TBAF showed that a) λ_{max}^{CL} was observed at 501 nm and the values of Φ^{CL} were one-figure higher than in the case of BTPP regardless of the concentration of TBAF, and b) $t_{1/2}$ increased as the concentration of

TBAF decreased. These results strongly suggest that, in the TBAF (200 eq.) system, **3c** formed di-oxido anion **13** of dioxetane which decomposed as rapidly as, or more quickly than, in the case in the BTPP system, and led to the excited mono-oxido anion of keto ester **12c** rather than the excited di-oxido anion **14**. This notable difference in the chemiexcitation of **3c** between the BTPP and TBAF systems presumably arises from how their conjugate acids, $(BTPP)H^+$ and HF or H_2O, operate through the BID. According to the mechanism typically proposed for CTID of an oxidoaryl-substituted dioxetane,[3,18,19,21] chemiluminescent decomposition of di-oxido anion **13** proceeds in the BTPP system as illustrated in Scheme 5, where singlet-chemiexcitation occurs as follows:

1) Intramolecular CT takes place from a dioxidophenyl to O-O in **13** to cause O-O bond cleavage to give transient diradical dianion **17** as an extreme structure.
2) Cleavage of the C-C bond in **17** gives singlet-excited di-oxido anion of ketoester **14**, which emits light with $\lambda_{max}^{CL} = 532$ nm.

The CTID of **13** should similarly proceed through **17** even in the TBAF system, though chemiluminescence occurs from mono-oxido anion **12c**, rather than from excited di-oxido anion **14**. We can presume here two possible pathways (A) and (B) through which **17** leads to excited mono-oxido anion **12c**. In pathway (A), excited di-oxido anion **14** is protonated to give excited mono-oxido anion **12c** prior to its deactivation, which emits light. However, pathway (A) could not be effective, since the excitation energy for **14** (λ_{max}^{CL}= 532 nm) would be lower than that for **12c** (λ_{max}^{CL} = 501 nm), though we



Scheme 5. Plausible singlet-chemiexcitation pathways for CTID of **3c** in a BTPP or TBAF system

cannot necessarily rule out that *de novo* **14** possibly possesses enough energy to form **12c**. On the other hand, in pathway (B), prior to C-C bond cleavage, transient **17** is protonated to give diradical anion **18**,

which decomposes to give excited **12c**. We should note that transient diradical dianion **17** may have a life-time long enough to become protonated.[21-23] In the TBAF system, small molecules H_2O and/or HF could easily access and donate a proton to **17**. On further reflection, in the BTPP system, di-oxido anion **13** presumably exists as a contact ion-pair with an extremely weak conjugate acid $(BTPP)H^+$, from which backward donation of H^+ to **17** may become far harder than in the TBAF system. Thus, as illustrated in Scheme 5, throughout BID starting from **13** to excited **14** in the BTPP system, all di-oxido anion species would be stabilized as a contact ion-pair. We should note here that differences in the response to TBAF between **2c** and **3c** are presumably due to the difference in the ease of dissociation of two phenolic OH groups between the 4-(benzoxazol-2-yl)-3,5-dihydroxyphenyl and 4-(*N*-phenylbenzimidazol-2-yl)-3,5-dihydroxyphenyl moieties.[24]

CONCLUSION

Chemiluminescent decomposition of dioxetanes **3a**−**3c** was effectively induced by organic superbases BTPP, TBD, MTBD, DBU, and TMG as well as TBAF in acetonitrile. TBD induced CTID of **3c** to give a flash of light (λ_{max}^{CL} = 520 nm). Furthermore, TBD enhanced the chemiluminescence efficiency, the value of which was 10-fold greater than that in the BTPP system, and also accelerated the rate of decomposition. This unique effect of TBD was suggested to arise from its "bifunctional" character, which led to the formation of a contact ion-pair complex as in **15**. On the other hand, TBAF caused the effective emission of blue light (λ_{max}^{CL} = 501 nm) from mono-oxido anion **12c** as in the case of a weaker base such as DBU or TMG, though it acted as a stronger base than BTPP with regard to the rate of decomposition of **3c**. The notable difference between TBAF and BTPP as a trigger for BID of **3c** was suggested to be due to whether or not intermediary di-oxido anion **13** could be stabilized through the formation of a contact ion-pair.

EXPERIMENTAL

General Melting points were uncorrected. IR spectra were taken on a FT/IR infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on a 600 MHz spectrometers. Mass spectra were obtained using a double-focusing mass spectrometer and an ESI-TOF mass spectrometer.

Synthesis of 4-(4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-2,6-dimethoxybenzaldehyde (5): BuLi (1.6 M in hexane, 4.7 mL, 7.6 mmol, 1.1 eq.) was added to a solution of 4-*tert*-butyl-5-(3,5-dimethoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**4**) (1.98 g, 6.82 mmol) in dry THF (20 mL) under N_2 atmosphere at 0 °C. The solution was stirred for 30 min and cooled to -78 °C. To the solution, dry DMF (0.80 mL, 10.3 mmol, 1.5 eq.) was added, stirred for 10 min and quenched with small amount of water. The reaction mixture was poured into sat. aq. NH_4Cl and extracted with AcOEt. The organic layer was

washed twice with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1 : 2) to give 2.02 g of **5** in 93% yield. **5**: Colorless granules, mp 68.0−69.5 °C (from hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.09 (s, 9H), 1.35 (s, 6H), 3.91 (s, 8H), 6.52 (s, 2H), 10.49 (s, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 27.3, 32.3, 32.4, 47.3, 56.1, 83.3, 105.7, 113.7, 126.4, 143.9, 148.7, 161.6, 189.1 ppm. IR (KBr): $\tilde{\nu}$ 2960, 2868, 1685, 1597, 1561, 1228, 1129 cm^{-1}. Mass (*m/z*, %): 318 (M^+, 25), 304 (19), 303 (100), 247 (36), 193 (27). HRMS (ESI): 319.1907, calcd for $C_{19}H_{27}O_4$ $[M + H]^+$ 319.1909, 341.1723, calcd for $C_{19}H_{26}O_4Na$ $[M + Na]^+$ 341.1729.

Synthesis of 4-(4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-2,6-dihydroxybenzaldehyde (6): A solution of benzaldehyde **5** (5.02 g, 15.8 mmol) and sodium methanethiolate (95%, 5.46 g, 74.1 mmol, 4.7 eq.) in dry DMF (50 mL) was stirred under N_2 atmosphere at refluxing temperature for 20 min. The reaction mixture was poured into diluted aq. HCl and extracted with AcOEt. The organic layer was washed three times with sat. aq. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silicagel and eluted with AcOEt-hexane (1:3) to give 3.99 g of 4-(4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-2,6-dihydroxybenzaldehyde (**6**) as a colorless solid in 87% yield. **6**: Colorless granules, mp 106.0−107.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.10 (s, 9H), 1.33 (s, 6H), 3.90 (s, 2H), 6.31 (s, 2H), 10.26 (s, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 27.1, 32.2, 32.4, 47.3, 83.2, 109.7 (broad C×2), 109.9, 127.3, 145.8, 147.6, 160.9 (broad C×2), 193.9 ppm. IR (KBr): $\tilde{\nu}$ 3582, 3455, 2954, 2868, 1633, 1616, 1567, 1270, 1193 cm^{-1}. Mass (*m/z*, %): 290 (M^+, 23), 276 (18), 275 (100), 219 (42), 165 (28). HRMS (ESI): 291.1579, calcd for $C_{17}H_{23}O_4$ $[M + H]^+$ 291.1596, 313.1398, calcd for $C_{17}H_{22}O_4Na$ $[M + Na]^+$ 313.1416.

Synthesis of 4-*tert*-butyl-5-[3,5-dimethoxy-4-(*N*-phenylbenz[*d*]imidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (7): According to the procedure reported,[25] a solution of benzaldehyde **5** (982 mg, 3.08 mmol) and *N*-phenyl-*o*-phenylenediamine (584 mg, 3.17 mmol, 1.0 eq.) in DMF (28.5 mL) and water (3 mL) was stirred at 80 °C for 4 h under aerobic conditions. The reaction mixture was poured into sat. aq. NaCl and extracted with AcOEt. The organic layer was washed three times with sat. aq. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1 : 2) to give 1.38 g of **7** as a colorless solid in 93% yield. **7**: Colorless needles, mp 218.0−220.0 °C (from AcOEt−hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.33 (s, 6H), 3.62 (s, 6H), 3.88 (s, 2H), 6.43 (s, 2H), 7.23−7.34 (m, 8H), 7.90 (d, J = 7.9 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 27.4, 32.3, 32.4, 47.2, 55.7, 83.2, 105.4, 108.5, 110.2, 120.1, 122.1, 122.7, 126.0, 126.1, 127.8, 128.8, 135.8, 136.4, 139.5, 143.5, 147.7, 149.3, 158.7 ppm. IR (KBr): $\tilde{\nu}$ 2956, 2861, 1607, 1574, 1237, 1130 cm^{-1}. Mass (*m/z*, %): 482 (M^++1, 32), 482 (M^+, 96), 481 (22), 468 (32), 467 (100), 451 (10), 411

(34), 357 (10). HRMS (ESI): 483.2641, calcd for $C_{31}H_{35}N_2O_3$ $[M + H]^+$ 483.2648.

Synthesis of 4-*tert*-butyl-5-[3-hydroxy-5-methoxy-4-(*N*-phenylbenz[*d*]imidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (9): A solution of dihydrofuran **7** (1.38 g, 2.86 mmol), and sodium methanethiolate (95%, 1.15 g, 15.6 mmol, 5.5 eq.) in dry DMF (50 mL) was stirred under N_2 atmosphere at 140 °C for 3.5 h. The reaction mixture was poured into diluted aq. HCl and extracted with AcOEt. The organic layer was washed three times with sat.aq. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1 : 2) to give 1.24 g of **9** as a colorless solid in 93% yield. **9**: Colorless granules, mp 202.5−204.0 °C (from acetone). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.09 (s, 9H), 1.32 (s, 6H), 3.03 (s, 3H), 3.88 (s, 2H), 6.13 (d, J = 1.3 Hz, 1H), 6.73 (d, J = 1.3 Hz, 1H), 7.24−7.31 (m, 3H), 7.33−7.38 (m, 2H), 7.40−7.45 (m, 3H), 7.83 (dd, J = 8.0 and 0.6 Hz, 1H), 10.88 (br-s, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 27.3, 32.3, 32.4, 47.1, 54.2, 83.2, 103.6, 103.7, 110.5, 111.6, 119.1, 123.1, 123.6, 125.1, 125.9, 127.6, 129.2, 135.5, 138.2, 140.1, 141.6, 149.1, 149.2, 156.0, 157.8 ppm. IR (KBr): $\tilde{\nu}$ 3426, 3064, 2957, 2859, 1618, 1582, 1223, 1099 cm^{-1}. Mass: *m/z* (%) 469 (M^+ + 1, 29), 468 (M^+, 90), 454 (31), 453 (100), 426 (15), 425 (48), 421 (15), 397 (30). HRMS (ESI): 469.2481, calcd for $C_{30}H_{33}N_2O_3$ $[M + H]^+$ 469.2491

Synthesis of 4-*tert*-butyl-5-[3,5-dihydroxy-4-(*N*-phenylbenz[*d*]imidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (8): A solution of benzaldehyde **6** (1.40 g, 4.82 mmol) and *N*-phenyl-*o*-phenylenediamine (942 mg, 5.11 mmol, 1.1 eq.) in DMF (48 mL) and water (6 mL) was stirred at 80 °C for 6 h under aerobic conditions and then stirred at room temperature overnight. The reaction mixture was poured into sat. aq. NaCl and extracted with AcOEt. The organic layer was washed three times with sat.aq. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−CH_2Cl_2 hexane (1 : 2) to give 1.92 g of **8** as a colorless solid in 88% yield. **8**: Colorless needles, mp 140.0−142.5 °C (from CH_2Cl_2−hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.28 (s, 6H), 3.79 (s, 2H), 6.32 (s, 2H), 7.22−7.29 (m, 3H), 7.31−7.36 (m, 4H), 7.38 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 27.2, 32.2, 32.4, 47.1, 83.0, 104.0, 110.4, 110.6, 119.1, 123.2, 123.6, 125.7, 126.3, 127.8, 129.1, 135.7, 137.4, 139.5, 141.7, 148.5, 148.9, 155.4 ppm. IR (KBr): $\tilde{\nu}$ 3640, 3531, 3409, 2958, 2871, 1618, 1594, 1210, 1054 cm^{-1}. Mass: *m/z* (%) 455 (M^+ + 1, 24), 454 (M^+, 72), 440 (31), 439 (100), 421 (20), 412 (14), 411 (49), 384 (12), 383 (46), 235 (24). HRMS (ESI): 455.2309, calcd for $C_{29}H_{31}N_2O_3$ $[M + H]^+$ 455.2335.

Synthesis of 5-*tert*-butyl-1-[3-hydroxy-5-methoxy-4-(*N*-phenylbenz[*d*]imidazole-2-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (3b): Typical procedure. A solution of dihydrofuran **9** (322 mg, 0.687 mmol) and Rose Bengal (3.6 mg) in AcOEt (30mL) was irradiated externally with 940 W Na lamp under O_2 atmosphere at 0 °C for 2 h. The photolysate was concentrated *in vacuo*. The residue

was chromatographed on silica gel and eluted with AcOEt−hexane (3 : 1) at low temperature to give 325 mg of **3b** as a colorless solid in 95% yield.

3b: Colorless needles, mp 133.5−137.5 °C (dec.) (from CH_2Cl_2−hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.15 (s, 3H), 1.36 (s, 3H), 3.05 (s, 3H), 3.82 (d, *J* = 8.2 Hz, 1H), 4.58 (d, *J* = 8.2 Hz, 1H), 6.54 (br-s, 1H), 7.01 (br-s, 1H), 7.21−7.45(m, 8H), 7.84 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 18.4, 25.0, 27.0, 36.8, 45.6, 54.3, 80.3, 102.1, 104.8, 105.3, 110.1, 110.6, 116.2, 119.2, 123.2, 123.8, 125.0, 127.8, 129.2, 135.5, 138.1, 140.0, 141.6, 148.8, 156.1, 157.9 ppm. IR (KBr): $\tilde{\nu}$ 3417, 3064, 2966, 2926, 1633, 1590, 1257, 1002 cm^{-1}. Mass: *m/z* (%) 501 (M^+ + 1, 33), 500 (M^+, 100), 468 (3), 343 (31), 329 (13), 316 (27), 315 (19), 300 (11), 243 (12), 57 (14). HRMS (ESI): 501.2369, calcd for $C_{30}H_{33}N_2O_5$ $[M + H]^+$ 501.2390.

5-*tert*-Butyl-1-[3,5-dihydroxy-4-(*N*-phenylbenz[*d*]imidazol-2-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (3c): 3c: 93% yield. Colorless needles, mp 148−149 °C (dec.) (from CH_2Cl_2−hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.96 (s, 9H), 1.09 (s, 3H), 1.27 (s, 3H), 3.73 (d, *J* = 8.2 Hz, 1H), 4.47 (d, *J* = 8.2 Hz, 1H), 6.67 (s, 2H), 7.21−7.39 (m, 8H), 7.76 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 18.3, 24.8, 26.9, 36.7, 45.5, 80.2, 104.5, 105.6, 108.4, 110.7, 116.1, 119.2, 123.3, 123.8, 125.5, 128.0, 129.2, 135.6, 137.3, 139.7, 141.6, 148.5, 155.5 ppm. IR (KBr): $\tilde{\nu}$ 3064, 2961, 2930, 1629, 1578, 1213, 1111 cm^{-1}. Mass: *m/z* (%) 487 (M^+ + 1, 32), 486 (M^+, 100), 454 (6), 386 (13), 346 (11), 330 (19), 329 (78), 302 (46), 301 (21), 273 (27), 245 (10), 243 (11), 235 (11), 57 (22). HRMS (ESI): 487.2208, calcd for $C_{29}H_{31}N_2O_5$ $[M + H]^+$ 487.2233.

Synthesis of 2,2,4,4-tetramethyl-3-oxopentyl 3-hydroxy-5-methoxy-4-(*N*-phenylbenz[*d*]imidazol-2-yl)benzoate (10b): Typical procedure. A solution of dioxetane **3b** (51 mg, 0.102 mmol) in *p*-xylene (2 mL) was refluxed for 130 min. After cooling, the reaction mixture was concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (3:1) to give 50 mg of **10b** as a solid.

10b: Colorless granules, mp 207.0−209.0 °C (from AcOEt−hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.40 (s, 6H), 3.06 (s, 3H), 4.38 (s, 2H), 6.82 (d, *J* = 1.4 Hz, 1H), 7.22−7.25 (m, 2H), 7.29−7.33 (m, 1H), 7.34 (d, *J* = 1.4 Hz, 1H), 7.35−7.49 (m, 5H), 7.85 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 23.6, 28.1, 45.9, 49.1, 54.3, 72.5, 102.5, 107.8, 110.7, 111.1, 119.3, 123.4, 124.0, 125.0, 127.9, 129.4, 133.2, 135.5, 138.1, 141.4, 148.5, 156.4, 158.4, 165.7, 216.0 ppm. IR (KBr): $\tilde{\nu}$ 3421, 3352, 2975, 1720, 1686, 1578, 1235, 1215, 1107 cm^{-1}. Mass: *m/z* (%) 501 (M^++1, 33), 500 (M^+, 100), 468 (3), 343 (35), 329 (13), 316 (29), 315 (21), 300 (12), 243 (14), 57 (19). HRMS (ESI): 501.2382, calcd for $C_{30}H_{33}N_2O_5$ $[M + H]^+$ 501.2390.

Synthesis of 2,2,4,4-tetramethyl-3-oxopentyl 3,5-dihydroxy-4-(*N*-phenylbenz[*d*]imidazol-2-yl)-benzoate (10c): Colorless needles, mp 137.0−139.0 °C (from AcOEt−hexane). ^{1}H NMR (600 MHz,

$CDCl_3$): δ_H 1.22 (s, 9H), 1.33 (s, 6H), 4.28 (s, 2H), 6.93 (s, 2H), 7.25−7.40 (m, 8H), 7.75 (d, J = 7.9 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 23.5, 28.0, 45.9, 49.1, 72.3,108.5, 109.1, 110.8, 119.2, 123.2, 123.8, 125.7, 128.1, 129.3, 132.8, 135.7, 137.1, 141.5, 148.3, 156.2,165.8, 217.0 ppm. IR (KBr): $\tilde{\nu}$ 3394, 2974, 1720, 1686, 1594, 1234, 1056 cm^{-1}. Mass: *m/z* (%) 487 (M^++1, 31), 486 (M^+, 100), 386 (12), 346 (10), 330 (16), 329 (73), 302 (38), 301 (18), 273 (22), 243 (11), 57 (20). HRMS (ESI): 487.2222, calcd for $C_{29}H_{31}N_2O_5$ $[M + H]^+$ 487.2233.

Chemiluminescence measurement: general procedure. Chemiluminescence was measured by using JASCO FP-6500 spectrometers and/or Hamamatsu Photonics PMA-11 multi-channel detector. Freshly prepared solution (2 mL) of a base (1.0 x 10^{-2} mol dm^{-3}) in MeCN was transferred to a quartz cell (10 x 10 x 50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C or 45 °C. After 3-5 min, a solution (1 mL) of the dioxetane (1.0 x 10^{-4} mol dm^{-3}) in MeCN, which was thermostated at the same temperature as that of the above base solution, was added with a syringe with immediate starting of measurement. The intensity of the light emission time-course was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with that of an adamantylidene dioxetane, whose chemiluminescent efficiency Φ^{CL} has been reported to be 0.29 and was used here as a standard.[13,14]

Fluorescence spectra of authentic keto esters 10a−10c: general procedure. A solution of the keto ester (1.0 x 10^{-4} mol dm^{-3}) and a base (1.0 x 10^{-2} mol dm^{-3}) in MeCN was measured at 25 °C by using JASCO FP-6200 spectrometer.

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