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Solvent effect on base-induced chemiluminescent decomposition of bicyclic dioxetanes bearing a 3-hydroxyphenyl group

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ABSTRACT

Chemiluminescent decomposition of dioxetanes bearing a 3-oxidophenyl was investigated in various solvents. The solvent-dependency of chemiluminescence efficiency Φ^{CL} showed a hierarchy that could be stratified into three classes: Φ^{CL} in aprotic polar solvents » in alcohols » in water. Hydrogen bond donor ability of the solvent was mainly responsible to the hierarchy. Singlet-chemiexcitation efficiency was less sensitive to the solvent than fluorescence efficiency of the emitter.

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1. Introduction

The base-induced decomposition (BID) of a dioxetane bearing an oxyaryl group proceeds through an unstable dioxetane bearing an oxidoaryl anion to produce a singlet-excited carbonyl fragment while effectively emitting light by an intramolecular CTID (charge-transfer induced decomposition) mechanism (Scheme 1) [1–9]. Thus, chemiluminescence based on oxyaryl-substituted dioxetanes is widely used in various biological and clinical applications [10–13]. Adamantylidene-substituted dioxetane **ADD** and bicyclic dioxetane **BCD** are basic models, which effectively emit light in an aprotic polar solvent, though they give quite weak light in water [14–19].

To overcome this significant defect, a wide variety of dioxetanes have recently been designed on the basis of two strategies: tethering of a fluorescer such as fluorescein to the 3-oxyphenyl group or to a substituent on the dioxetane ring of **ADD** or **BCD** [20,21], and the introduction of a functionalized π-conjugation system to the 3-oxyphenyl group of **ADD** or **BCD** [22–31]. However, it is not yet clear how water markedly decreases Φ^{CL} (chemiluminescence efficiency) for the BID of dioxetanes such as **ADD** and **BCD**, though hydrogen-bonding (HB) and dipole-dipole interaction have been suggested to presumably be responsible for these decreases in an aqueous system [22,32,33].

Against this background, we sought to understand with the help of LSER (linear solvation energy relationships) analysis [34,35] how the solvent affected BID of oxyaryl-substituted dioxetanes. In addition to parent **1a** (**BCD**: Y = H), we examined three bicyclic dioxetanes bearing a 3-hydroxyphenyl substituted with 4-phenyl **1b**, biphenyl-4-yl **1c**, or *N*-methylbenzimidazol-2-yl **2**. Chemiluminescent BID effectively occurs for all of these dioxetanes in an aprotic polar solvent such as acetonitrile (AN) (Φ^{CL} = 0.1–0.2), whereas their Φ^{CL} values in water are markedly different from each other by an order of magnitude, from 10^{-5} to 10^{-2} in the order **1a** < **1b** < **1c** < **2** (Fig. 1) [17,33,36]. On the other hand, for some reason little is known about BID for oxyaryl-substituted dioxetanes in a protic solvent other than water, such as alcohols. Thus, we selected five typical alcohols, *t*-BuOH (tertiary), *i*-PrOH (secondary), and BuOH, EtOH, and MeOH (primary) in addition to water and three aprotic polar solvents, DMSO, DMF, and AN, as solvents for this investigation.

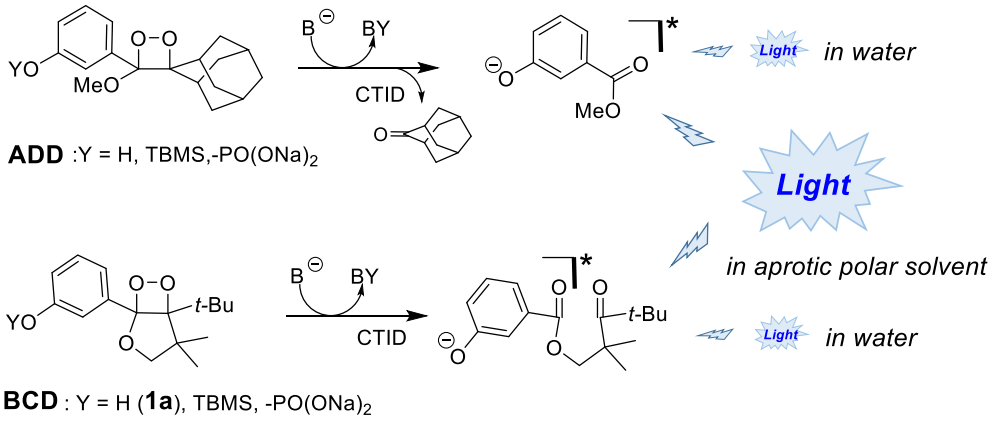
2. Results and discussions

2.1. Solvent effect on the chemiluminescent BID of oxyphenyl-substituted dioxetanes

BID of oxyaryl-substituted dioxetanes has been carried out, in

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Scheme 1. Base-induced chemiluminescent decomposition of oxyaryl-substituted dioxetanes **ADD** and **BCD**.

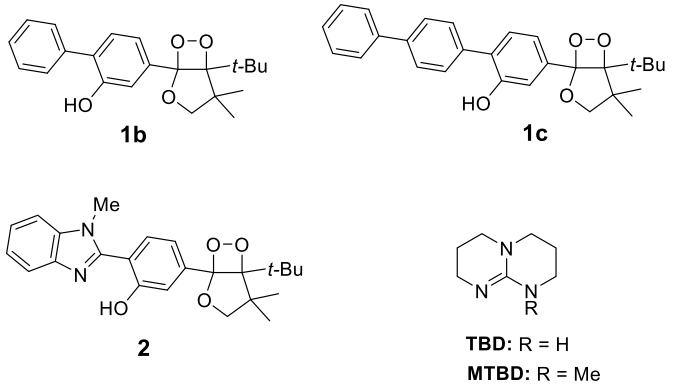


Fig. 1. Bicyclic dioxetanes bearing a 3-hydroxyphenyl substituted with 4-phenyl **1b**, biphenyl-4-yl **1c**, or *N*-methylbenzimidazol-2-yl **2**, and the super-base TBD and MTBD.

most cases, by using TBAF (tetrabutylammonium fluoride) as a trigger base in an aprotic polar solvent, while an alkaline metal hydroxide such as NaOH is used in water [10,15,32,33]. However, we chose here a strong base capable of acting as a common trigger in all of the nine solvents selected. The chosen base was TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), which is a well-known super-base (pKa = 26.0 in AN) [37–39] that has been reported to effectively mediate chemiluminescent BID of **1a** and benzoxazole-analogs of **2** in AN [40].

When parent dioxetane **1a** (3.3×10^{-5} M) was treated with a large excess of TBD (200 eq.) in DMSO at 25 °C, **1a** rapidly decomposed to keto ester **3a** according to pseudo-first-order kinetics accompanied by the emission of blue light with maximum wavelength $\lambda_{max}^{CL} = 470$ nm, rate of BID $k^{BID} = 5.4 \times 10^{-2}$ s^{-1}, and $\Phi^{CL} = 0.21$ [41,42] (Table 1 and Fig. 2(A)). These Φ^{CL} and λ_{max}^{CL} values practically coincided with those for BID of **1a** using TBAF [17,19]. Next, we investigated the TBD-mediated chemiluminescent BID of **1a** in two aprotic polar solvents (DMF and AN), five alcohols (*t*-BuOH, *i*-PrOH, BuOH, EtOH, and MeOH), and water. BID in DMF and AN was carried out as in DMSO. On the other hand, BID in the five alcohols and water was conducted at an elevated temperature, 45 °C, to accelerate the reaction rate and increase the intensity of light emission. Furthermore, a higher concentration of **1a** and 200 eq. of TBD was used in these solvent systems: 1.7×10^{-4} M of **1a** in *t*-BuOH, *i*-PrOH, BuOH, and EtOH, and 3.3×10^{-4} M of **1a** in MeOH and water. The results are summarized in Table 1 and the chemiluminescence spectra are shown in Fig. 2 (A).

The results in Table 1 show that, for BID of parent **1a**, i) λ_{max}^{CL} in

Table 1
Base-induced chemiluminescent decomposition of dioxetane **1a**[a].

solvent	λ_{max}^{CL}/nm	Φ^{CL}[b]	k^{BID}/s^{-1}
DMSO[c]	470 (471)	0.21 (0.20)	$5.4\ (15) \times 10^{-2}$
DMF	470	0.16	2.3×10^{-2}
AN[c]	472(471)	0.14 (0.11)	$3.1\ (2.5) \times 10^{-2}$
t-BuOH	480	3.5×10^{-3}	1.8×10^{-3}
i-PrOH	480	1.6×10^{-3}	2.9×10^{-3}
BuOH	480	9.1×10^{-4}	1.9×10^{-3}
EtOH	482	5.5×10^{-4}	1.7×10^{-3}
MeOH	483	2.3×10^{-4}	4.8×10^{-4}
Water[d]	490 (467)	$1.6\ (1.1) \times 10^{-5}$	$6.8 \times 10^{-3}\ (8.6 \times 10^{-4})$

[a] In DMSO, DMF, and AN systems, dioxetane **1a** (3.3×10^{-5} M) was treated with TBD (200 eq.) at 25 °C. In *t*-BuOH, *i*-PrOH, BuOH, and EtOH systems, dioxetane **1a** (1.7×10^{-4} M) was treated with TBD (200 eq.) at 45 °C. In MeOH and water systems, dioxetane **1a** (3.3×10^{-4} M) was treated with TBD (200 eq.) at 45 °C.
[b] Based on a value reported for the chemiluminescent decomposition of **ADD** (Y = *t*-Bu(Me)$_2$Si: TBMS) in TBAF/DMSO [41,42].
[c] Values in parentheses were obtained using TBAF as a base [17,19].
[d] Values in parentheses were obtained using NaOH as a base [17].

aprotic polar solvent systems was ca 10–20 nm shorter than that in a protic system, ii) k^{BID} was large in aprotic polar solvents, significantly decreased in alcohols, and increased again in water, and iii) the solvent effect on Φ^{CL} showed a hierarchy: the nine solvents could be stratified into three classes, a) aprotic polar solvents ($\Phi^{CL} = 0.1$–0.2), b) alcohols ($\Phi^{CL} = 4 \times 10^{-3} - 2 \times 10^{-4}$), and c) water ($\Phi^{CL} = 2 \times 10^{-5}$). These notable features of the solvent effect on Φ^{CL} are illustrated in Fig. 3.

Next, we investigated the chemiluminescent BID of dioxetanes **1b** and **1c** as in the case of **1a** in the nine solvent systems: chemiluminescence spectra are shown in Fig. 2(B) and (C), and the chemiluminescence properties are summarized in Tables 2 and 3. The features of the solvent-dependency of Φ^{CL} are illustrated in Fig. 3. Based on the results in Table 2 and Fig. 3, for BID of **1b,** i) the Φ^{CL} values were high, as with **1a** in aprotic solvents, but significantly decreased by one to two orders of magnitude in alcohols, and decreased an additional order of magnitude in water, ii) this feature of the solvent effect on Φ^{CL} apparently showed a hierarchy similar to but not as prominent as in the case of **1a** (Fig. 3), iii) the solvent-dependency of λ_{max}^{CL} was similar to that in the case of **1a**, and iv) k^{BID} in aprotic polar solvents was at least an order of magnitude greater than that in protic solvents, and was an order of magnitude greater in water than in alcohols.

Table 3 for the BID of terphenyl-dioxetane **1c** shows that i) Φ^{CL} changed depending on the solvent as in the cases of **1a** and **1b** though the magnitude of the change was less (Fig. 3), and ii) k^{BID} was affected by the solvent as in the case of **1b**, while λ_{max}^{CL}, in

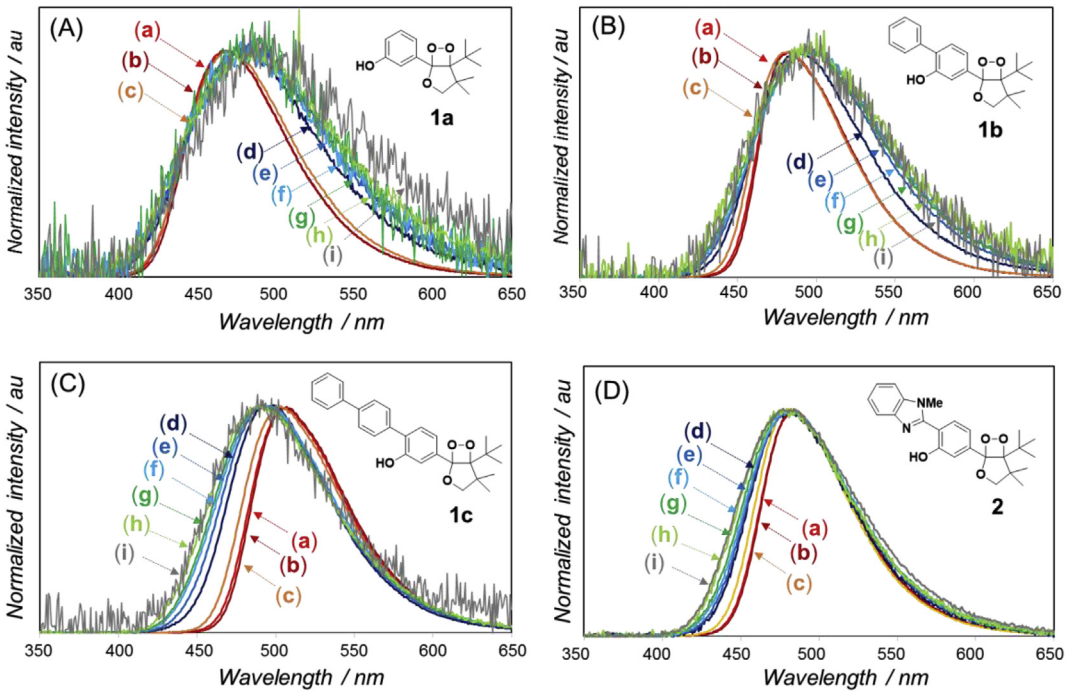


Fig. 2. Chemiluminescence spectra of dioxetanes **1a** (A), **1b** (B), **1c** (C), and **2** (D) in various solvents with the use of TBD: (a) DMSO, (b) DMF, (c) AN, (d) *t*-BuOH, (e) *i*-PrOH, (f) BuOH, (g) EtOH, (h) MeOH, and (i) water.

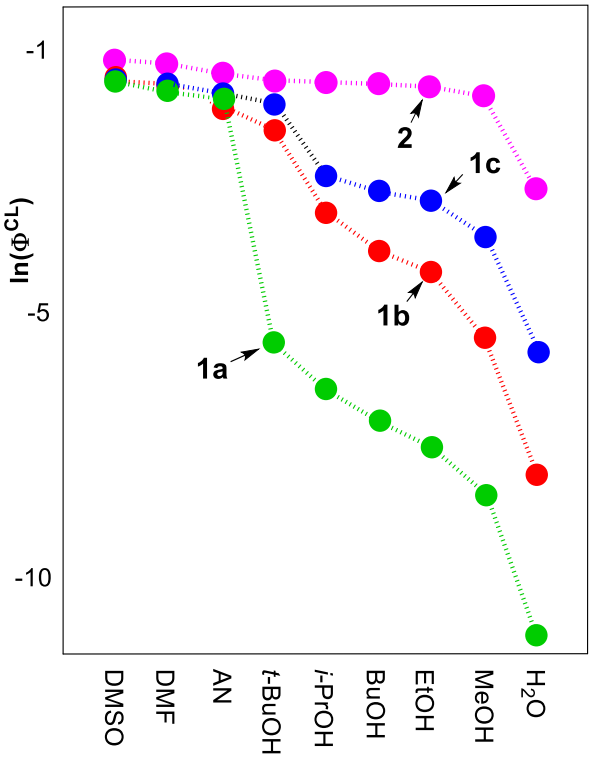


Fig. 3. Dependency of Φ^{CL} on solvent for the chemiluminescent BID of dioxetanes **1a**–**1c** and **2**.

contrast to the results with **1a** and **1b**, showed blue-shift from a protic solvent to an aprotic solvent.

BID of dioxetane **2** bearing a benzimidazolylphenol has been known to effectively emit light even in water, though the rate of BID is quite slow at 25 °C [36]. Thus, we carried out chemiluminescent BID of **2** with TBD at 45 °C rather than at 25 °C to increase the rate

Table 2
Base-induced chemiluminescent decomposition of dioxetane **1b**[a].

solvent	λ_{max}^{CL}/nm	Φ^{CL}[b]	k^{BID}/s^{-1}
DMSO[c]	483 (483)	0.24 (0.24)	$2.6\ (4.3) \times 10^{-1}$
DMF	484	0.19	1.2×10^{-1}
AN[c]	480 (482)	0.14 (0.18)	$1.2\ (1.7) \times 10^{-1}$
t-BuOH	489	8.2×10^{-2}	2.1×10^{-3}
i-PrOH	496	4.7×10^{-2}	3.5×10^{-3}
BuOH	497	2.1×10^{-2}	2.8×10^{-3}
EtOH	497	1.5×10^{-2}	2.9×10^{-3}
MeOH	497	4.5×10^{-3}	1.3×10^{-3}
Water[d]	493 (493)	$3.2\ (2.1) \times 10^{-4}$	$1.4\ (0.72) \times 10^{-2}$

[a] Dioxetane **1b** (3.3×10^{-5} M) was treated with TBD (200 eq.) at 25 °C.
[b] Based on a value reported for the chemiluminescent decomposition of **ADD** (Y = *t*-Bu(Me)$_2$Si: TBMS) in TBAF/DMSO [41,42].
[c] Values in parentheses were obtained using TBAF as a base [33].
[d] Values in parentheses were obtained using NaOH as a base [33].

Table 3
Solvent effect on the chemiluminescence properties of dioxetane **1c**[a].

solvent	λ_{max}^{CL}/nm	Φ^{CL}[b]	k^{BID}/s^{-1}
DMSO[c]	506 (506)	0.21 (0.22)	$2.5\ (3.6) \times 10^{-1}$
DMF	508	0.20	1.3×10^{-1}
AN[c]	500 (503)	0.16 (0.16)	$1.1\ (1.1) \times 10^{-1}$
t-BuOH	498	0.12	2.4×10^{-3}
i-PrOH	496	9.8×10^{-2}	3.8×10^{-3}
BuOH	495	6.7×10^{-2}	3.1×10^{-3}
EtOH	493	5.8×10^{-2}	3.1×10^{-3}
MeOH	488	2.6×10^{-2}	1.6×10^{-3}
Water[d]	493 (493)	$3.0\ (2.4) \times 10^{-3}$	$4.6\ (1.6) \times 10^{-3}$

[a] Dioxetane **1c** (3.3×10^{-5} M) was treated with TBD (200 eq.) at 25 °C.
[b] Based on a value reported for the chemiluminescent decomposition of **ADD** (Y = TBMS) in TBAF/DMSO [41,42].
[c] Values in parentheses were obtained using TBAF as a base [33].
[d] Values in parentheses were obtained using NaOH as a base [33].

Table 4
Solvent effect on the chemiluminescence properties of dioxetane **2**[a)].

solvent	λ_{max}^{CL}/nm	Φ^{CL}[b)]	k^{BID}/s^{-1}
DMSO	485	0.30	8.3×10^{-3}
DMF	485	0.26	5.9×10^{-3}
AN[c)]	482 (483)	0.23 (0.22)	$5.0\ (7.7) \times 10^{-3}$
t-BuOH	482	0.21	2.6×10^{-4}
i-PrOH	482	0.21	4.1×10^{-4}
BuOH	482	0.20	2.9×10^{-4}
EtOH	480	0.19	2.7×10^{-4}
MeOH	480	0.15	1.6×10^{-4}
Water[d)]	480 (480)	0.07 (0.024)	$1.8\ (1.9) \times 10^{-3}$

[a] Dioxetane **2** (3.3×10^{-5} M) was treated with TBD (200 eq.) at 45 °C.
[b] Based on a value reported for the chemiluminescent decomposition of **ADD** (Y = TBMS) in TBAF/DMSO [41,42].
[c] Values in parentheses were obtained using TBAF as a base [36].
[d] Values in parentheses were obtained using NaOH as a base [36].

and thus increase the intensity of light emission. The chemiluminescence spectra are shown in Fig. 2 (D) and chemiluminescence properties are summarized in Table 4: the features of the solvent-dependency of Φ^{CL} are illustrated in Fig. 3. As shown in Tables 4, i) Φ^{CL} of **2** decreased only gradually in alcohols in the order *t*-BuOH ≥ *i*-PrOH > BuOH > EtOH > MeOH and was rather effective even in water, ii) the features of the solvent-dependency of Φ^{CL} for **2** resembled those for **1a**–**1c** (*vide infra*, Fig. 3), iii) k^{BID} of **2** was the largest in water among protic solvents as in the cases of **1a**–**1c**, and iv) the solvent-dependency of λ_{max}^{CL} was similar to that in the case of **1c**, though the magnitude of the change was quite small.

In conclusion, chemiluminescent BID displayed a notable solvent effect on Φ^{CL} and k^{BID}, but not λ_{max}^{CL}, which was common to all of the dioxetanes **1a**–**1c** and **2**, even though these four dioxetanes showed marked differences in Φ^{CL} and k^{BID}, as follows:

i) The solvent effect on Φ^{CL} showed a hierarchy that could be stratified into three classes: high Φ^{CL} was attained in an aprotic polar solvent, while it moderately to significantly decreased in an alcohol and further decreased by an order of magnitude or more in water.
ii) k^{BID} was large in aprotic polar solvents, significantly decreased in alcohols, and increased again in water.

We will discuss below how the properties of the solvent affected Φ^{CL} and k^{BID} for the chemiluminescent BID of dioxetanes **1a**–**1c** and **2**.

2.2. LSER analysis of solvent effects on the chemiluminescence efficiency for BID of oxyphenyl-substituted dioxetanes

As shown in Fig. 3, the solvent effect on Φ^{CL} for BID of dioxetanes **1a**–**1c** and **2** did not appear to simply correlate with any properties of the solvent such as the polarity index or some other parameter such as the dielectric constant (ε), dipole moment (μ), polarity parameter (E^T), or nucleophilicity/electrophilicity parameter DN (donor number)/AN (acceptor number). Thus, we performed an LSER analysis according to the following equation [34,35]:

$$A = s\pi^* + a\alpha + b\beta + Ao \qquad \text{(eq. 1)}$$

where A is $\ln(\Phi^{CL})$, π^* is an index of solvent dipolarity/polarizability, α is a measure of the solvent hydrogen-bond donor (HBD) and Lewis-acidity, and β is a measure of the solvent hydrogen-bond acceptor (HBA) and Lewis-basicity, and A_0 is a constant term (see ESI).

First, LSER analysis was applied to the data of Φ^{CL} for all of the dioxetanes **1a**–**c** and **2**. A multivariate analysis of the data in Table 1–4 agreed with the results of LSER as shown in eq. (2)–5:

$$\ln\left(\Phi^{CL}\ for\ \mathbf{1a}\right) = -1.28\pi^* - 7.45\alpha + 1.02\beta - 1.24 \quad \left(R^2 = 0.996\right) \qquad \text{(eq. 2)}$$

$$\ln\left(\Phi^{CL}\ for\ \mathbf{1b}\right) = -2.41\pi^* - 4.52\alpha + 2.00\beta - 0.66 \quad \left(R^2 = 0.991\right) \qquad \text{(eq. 3)}$$

$$\ln\left(\Phi^{CL}\ for\ \mathbf{1c}\right) = -2.16\pi^* - 2.80\alpha + 1.14\beta - 0.38 \quad \left(R^2 = 0.986\right) \qquad \text{(eq. 4)}$$

$$\ln\left(\Phi^{CL}\ for\ \mathbf{2}\right) = -0.45\pi^* - 0.81\alpha + 0.57\beta - 1.27 \quad \left(R^2 = 0.950\right) \qquad \text{(eq. 5)}$$

Equation (2)–5 show negative coefficients for the π^* and α terms and a positive coefficient for the β term. Fig. 4 should help to explain the individual contributions of the three terms π^*, α and β to the solvent effect on Φ^{CL} for BID of dioxetanes **1a-1c** and **2**. For the BID of dioxetanes **1a**–**1c**, the LSER analysis suggested as follows (*vide infra* for **2**):

i) The dipolarity/polarizability (π^* term) and HBD ability/Lewis-acidity (α term) of the solvent synergistically decrease Φ^{CL} while the HBA ability/Lewis-basicity (β term) of the solvent competitively increases Φ^{CL}.
ii) The hierarchy for the dependency of Φ^{CL} on the solvent (Φ^{CL} in aprotic polar solvents » in alcohols » in water), which was significant especially for **1a**, is mainly attributed to the HBD ability/Lewis-acidity (α term) of the solvent: aprotic polar solvents have $\alpha = 0$, while protic solvents possess a higher α term (see also iii).
iii) The largest π^* and α, but the smallest β, for water among all of the solvents investigated are most likely responsible for the noticeable drop of Φ^{CL} in water.
iv) The finding that the solvent dependency of Φ^{CL} became less sensitive in the order **1a** > **1b** > **1c** is presumably due to the fact that the negative contribution of HBD ability/Lewis-acidity (α term) markedly decreases in the order **1a** > **1b** > **1c.**

Equation (5) for **2** shows relatively small coefficients for all three terms, π^*, α and β, compared to **1a**–**c** (eq. (2)–4). Thus, we can understand the result that the solvent slightly influenced Φ^{CL} for **2** (Table 4). As suggested by the LSER analysis, the finding that Φ^{CL} increased in the order **1a** < **1b** < **1c** ≪ **2** in water could be mainly attributed to the decrease in the negative contribution of the HBD ability/Lewis-acidity (α term) in the order **1a** > **1b** > **1c** » **2** (Fig. 4).

2.3. Solvent effects on the fluorescence efficiency of emitter and singlet chemiexcitation efficiency for BID of oxyphenyl-substituted dioxetanes

BID of oxyphenyl-substituted dioxetanes **1a**-**1c** and **2** has been known to selectively produce respective oxidobenzoates (emitters) **3a**–**3c** and **4**, which give the corresponding oxybenzoates **5a**–**5c** and **6** after neutralization (Scheme 2) [17,33,36]. Therefore, singlet-chemiexcitation efficiency Φ_S for BID is expressed as $\Phi_S = \Phi^{CL}/\Phi^{fl}$

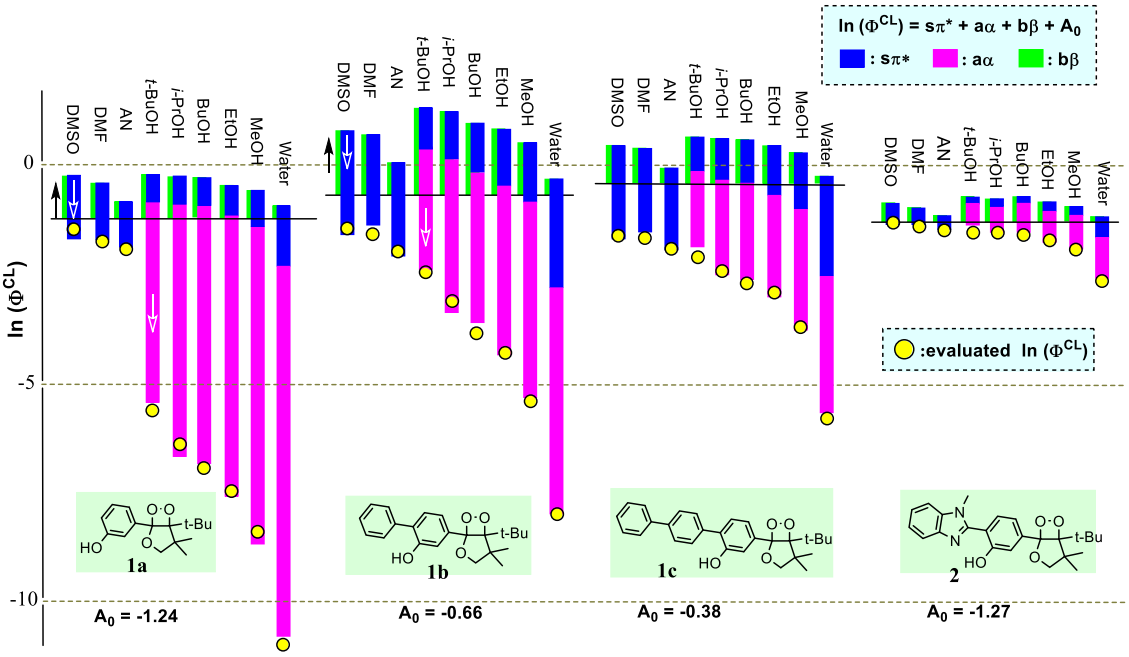


Fig. 4. Contributions of the π^*, α and β terms to the solvent effect on Φ^{CL} for BID of dioxetanes **1a-c** and **2**. "The symbol ↑ means that the term contributes to increase Φ^{CL}, while ↓ means that the term contributes to decrease Φ^{CL}."

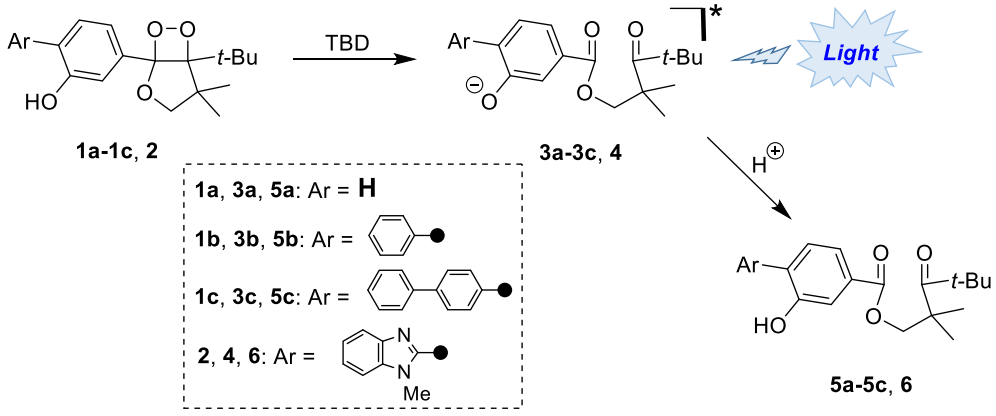
(Φ^{fl}: fluorescence efficiency of the emitter), so that it can be estimated through fluorescence measurement of the authentic emitters.

Thus, we first investigated how Φ^{fl} changed depending on the solvent used for BID of dioxetanes **1a**–**1c** and **2**. Although we attempted to measure Φ^{fl} of authentic emitters **3a**–**3c** and **4** in all of the nine solvent systems used for the present BID, we had to exclude an aqueous system for **3a** and **3b**, which hardly showed fluorescence with reliable reproducibility presumably because of their rapid hydrolysis [43,44]. Instead, we predicted Φ^{fl} of **3a** and **3b** in an aqueous system by an LSER analysis of the data for solvent systems except water.

The authentic emitters **3a**–**3c** and **4** were individually prepared by dissolving the corresponding keto esters **5a**–**5c** and **6** in a solvent that included a large excess of MTBD at 25 °C: MTBD (*N*-methyl-TBD: pKa = 25.5 in AN) [37–39] was used in place of TBD to avoid as much as possible change like amidation of the benzoates with TBD during fluorescence measurement (see ESI) [45]. The thus-prepared emitters **3a**–**3c** and **4** effectively showed fluorescence, the spectra of which practically coincided with the respective chemiluminescence spectra of **1a**–**1c** and **2**: the maximum wavelength of fluorescence λ^{fl}_{max} agreed with those of the corresponding λ^{CL}_{max} within <1% error, as shown in Table 5 (see ESI). The Φ^{fl} values of **3a**–**3c** and **4** are summarized together with the λ^{fl}_{max} values in Table 5. Fig. 5 shows the dependency of Φ^{fl} on the solvents.

Based on Table 5 and Fig. 5, the solvent effect on Φ^{fl} has the following features.

i) For **3a**, the Φ^{fl} values in aprotic polar solvents were high, while they significantly decreased in alcohols in the order *t*-BuOH > *i*-PrOH > BuOH ≥ EtOH > MeOH.
ii) For **3b**, the Φ^{fl} values decreased as in the case of **3a**, but the trend was gradual: Φ^{fl} in MeOH vs in DMSO for **3b** was 1/17, while that for **3a** was 1/140.
iii) For **3c** and **4**, Φ^{fl} was somewhat larger in alcohols, except MeOH, than in aprotic polar solvents, though it decreased slightly in the same order as in protic solvents. The Φ^{fl} values



Scheme 2. Base-induced chemiluminescent decomposition of bicyclic dioxetanes **1a**–**1c** and **2**.

Table 5
Fluorescence efficiency Φ^{fl} of authentic emitters **3a**–**3c** and **4**[a)].

solvent	3a		3b		3c		4	
	λ^{fl}_{max} /nm	Φ^{fl}	λ^{fl}_{max} /nm	Φ^{fl}	λ^{fl}_{max} /nm	Φ^{fl}	λ^{fl}_{max} /nm	Φ^{fl}
DMSO	470	0.32	481	0.42	503	0.36	482	0.65
DMF	470	0.27	482	0.36	504	0.34	481	0.57
AN	472	0.24	481	0.25	496	0.27	480	0.49
t-BuOH	476	1.3×10^{-2}	486	0.26	495	0.53	479	0.68
i-PrOH	476	7.1×10^{-3}	493	0.19	495	0.48	479	0.61
BuOH	476	4.8×10^{-3}	493	0.11	495	0.44	479	0.65
EtOH	477	4.1×10^{-3}	493	7.5×10^{-2}	495	0.35	479	0.59
MeOH	479	2.3×10^{-3}	493	2.5×10^{-2}	495	0.20	478	0.50
Water	———[b)]	(1.3×10^{-3})[c)]	———[b)]	(2.7×10^{-3})[c)]	493	3.7×10^{-2}	477	0.23

[a] Fluorescence was measured at 25 °C.
[b] Not measured.
[c] Predicted values based on LSER analysis shown in eqs. (6) and (7).

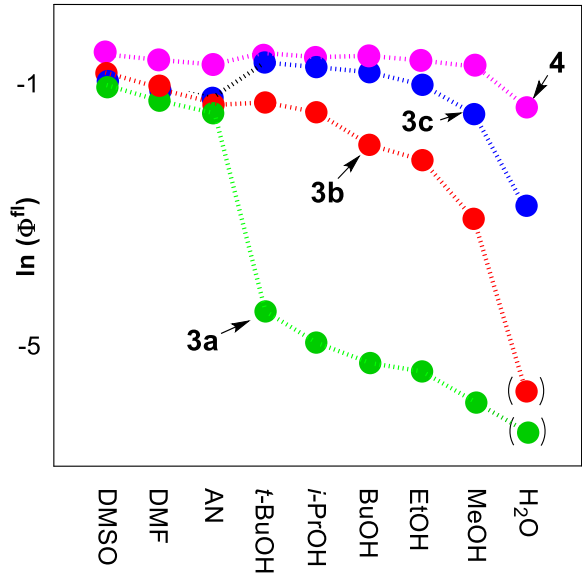


Fig. 5. Dependency of Φ^{fl} on the solvent for emitters **3a**–**3c** and **4**. "The mark ( ) means the predicted Φ^{fl}."

for **3c** and **4** were high in MeOH but considerably decreased in water.

Next, we conducted LSER analysis of Φ^{fl} for **3a-3c** and **4**: the data for **3a** and **3b** were obtained in eight solvent systems, excluding a water system. The results of a multivariate analysis of the data in Table 5 were well correlated with LSER as shown in eq. (6)–9: the Φ^{fl} values for **3a** and **3b** in a water system were predicted from eqs. (6) and (7) (Table 5 and Fig. 5).

$$\ln\left(\Phi^{fl}\ for\ \mathbf{3a}\right) = 0.70\pi^* - 4.68\alpha + 0.45\beta - 2.19 \quad \left(R^2 = 0.998\right) \qquad \text{(eq. 6)}$$

$$\ln\left(\Phi^{fl}\ for\ \mathbf{3b}\right) = -2.16\pi^* - 3.22\alpha + 1.90\beta - 2.19 \quad \left(R^2 = 0.966\right) \qquad \text{(eq. 7)}$$

$$\ln\left(\Phi^{fl}\ for\ \mathbf{3c}\right) = -1.91\pi^* - 1.13\alpha + 1.11\beta - 0.06 \quad \left(R^2 = 0.981\right) \qquad \text{(eq. 8)}$$

$$\ln\left(\Phi^{fl}\ for\ \mathbf{4}\right) = -0.57\pi^* - 0.42\alpha + 0.61\beta - 0.42 \quad \left(R^2 = 0.944\right) \qquad \text{(eq. 9)}$$

The contributions of the π^*, α and β terms to a solvent effect on Φ^{fl} are shown in Fig. 6. Thus, referring to the LSER analysis (eq. (6)–9, Fig. 6), the solvent effects on Φ^{fl} of **3a**–**3c** and **4** can be described as follows.

i) HBD ability/Lewis-acidity (α term) of the solvent decreases Φ^{fl}, while HBA ability/Lewis-basicity (β term) of the solvent competitively increases Φ^{fl}.
ii) HBD ability/Lewis-acidity (α term) of the solvent predominantly decreases Φ^{fl} for **3a.** However, the contribution of the α term diminishes in the order **3a** > **3b** > **3c** > **4.**
iii) Dipolarity/polarizability (π^* term) and HBA ability/Lewis-basicity (β term) of the solvent compete with each other except for the case of **3a**, though the negative π^* term greatly exceeds the positive β term especially in water and AN systems for **3b** and **3c** (Fig. 6).
iv)ιϖ)Φ^{fl} for **4** is far less sensitive than those for **3a**–**3c** to all of the three categories of solvent.

Next, we estimated singlet-chemiexcitation efficiencies $\Phi_S = \Phi^{CL}/\Phi^{fl}$ for BID of dioxetanes **1a-c** and **2** from Φ^{CL} and Φ^{fl} in Table 1–5 The results are summarized in Table 6 and illustrated in Fig. 7:

i) In comparing Φ_S to Φ^{fl}, the most noticeable point was that the solvent-dependency of Φ_S was far less sensitive than that of Φ^{fl}, and the Φ_S values were considerably large even in MeOH for **1a** and **1b**, in contrast to the case of Φ^{fl}: Φ_S in MeOH vs in DMSO was ca. 1/7 for **1a**, while Φ^{fl} in MeOH vs in DMSO was ca. 1/140 for the corresponding emitter **3a.**
ii) Φ_S gradually decreased for all of the dioxetanes in the order DMSO > DMF ≥ (≤) AN > *t*-BuOH ≥ *i*-PrOH > BuOH ≥ (≤) EtOH > MeOH.
iii) The effect of water decreasing Φ_S was prominent for all of the cases except **2** (see Fig. 7).

As with Φ^{CL} and Φ^{fl}, we carried out LSER analysis of Φ_S for BID of

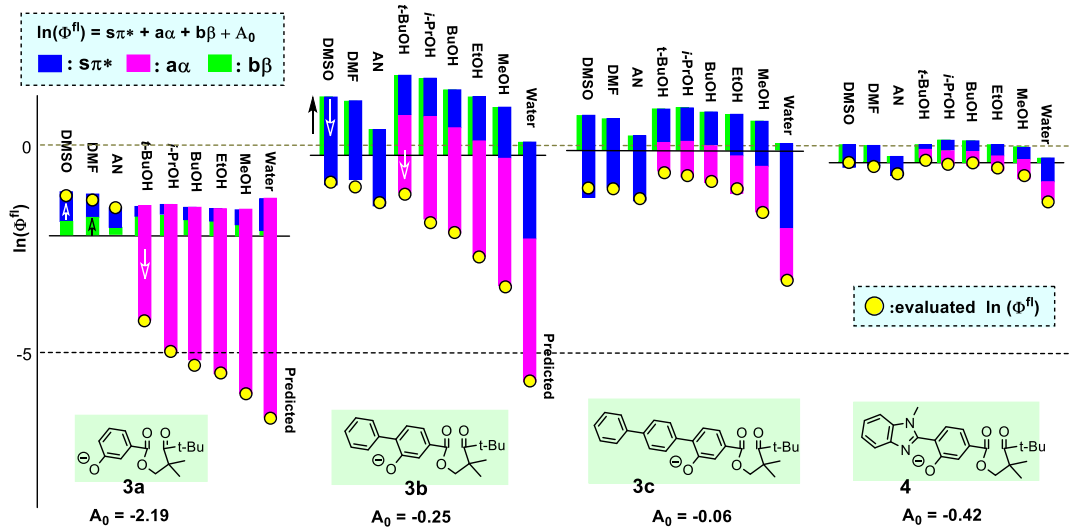


Fig. 6. Contributions of the π^*, α and β terms to the solvent effect on Φ^{fl} for emitters **3a**–**3c** and **4** "The symbol ↑ means that the term contributes to increase Φ^{fl}, while ↓ means that the term contributes to decrease Φ^{fl}."

Table 6
Singlet-chemiexcitation efficiency Φ_S for BID of dioxetanes **1a**–**1c** and **2** in various solvents.

solvent	1a	1b	1c	2
DMSO	0.66	0.57	0.58	0.46
DMF	0.59	0.53	0.59	0.46
AN	0.58	0.56	0.59	0.47
t-BuOH	0.27	0.32	0.23	0.31
i-PrOH	0.23	0.25	0.20	0.34
BuOH	0.19	0.19	0.15	0.31
EtOH	0.13	0.20	0.17	0.32
MeOH	0.10	0.18	0.13	0.30
Water	(0.012)[a)]	(0.12)[a)]	0.08	0.30

[a] Figures in parenthesis mean the value based on the Φ^{fl} values predicted according to eqs. (6) and (7).

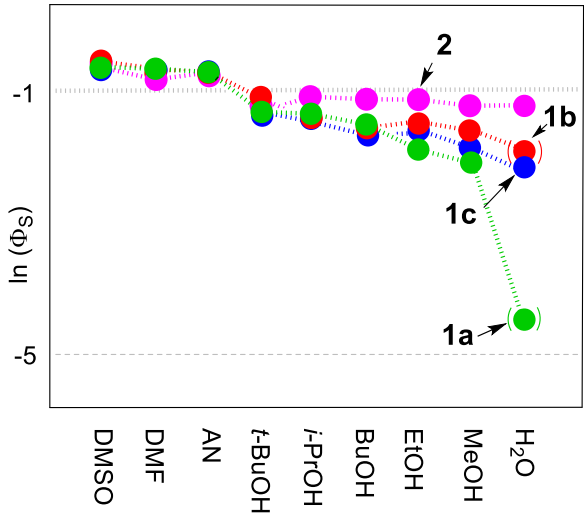


Fig. 7. Dependency of Φ_S on solvent for the chemiluminescent BID of dioxetanes **1a**–**1c** and **2.** "The mark () means the predicted Φ_S."

dioxetanes **1a-1c** and **2**. The results of a multivariate analysis of the data in Table 6 were also consistent with LSER.

$$\ln(\Phi_S \textit{ for } \mathbf{1a}) = -2.00\pi^* - 2.78\alpha + 0.57\beta + 0.96 \quad (R^2 = 0.978) \quad \text{(eq. 10)}$$

$$\ln(\Phi_S \textit{ for } \mathbf{1b}) = -0.22\pi^* - 1.28\alpha + 0.10\beta - 0.45 \quad (R^2 = 0.978) \quad \text{(eq. 11)}$$

$$\ln(\Phi_S \textit{ for } \mathbf{1c}) = -0.24\pi^* - 1.66\alpha + 0.05\beta - 0.35 \quad (R^2 = 0.987) \quad \text{(eq. 12)}$$

$$\ln(\Phi_S \textit{ for } \mathbf{2}) = 0.09\pi^* - 0.40\alpha - 0.06\beta - 0.82 \quad (R^2 = 0.962) \quad \text{(eq. 13)}$$

According to eq. (10)–13, the contributions of the π^*, α and β terms to the solvent effect on Φ_S are shown in Fig. 8, which explains how the solvents affect Φ_S for BID of **1a-c** and **2**:

i) HBD ability/Lewis-acidity (α term) of the solvent practically dominates the solvent effect decreasing Φ_S, though the absolute contribution of the α term decreasing Φ_S decreases in the order **1a** < **1b** ≤ **1c** < **2.**
ii) For all cases, the contribution of the α term to the decrease in Φ_S increases in the order *t*-BuOH < *i*-PrOH < BuOH ≤ EtOH < MeOH < water.
iii) Compared to the case of Φ^{fl}, the HBD ability/Lewis-acidity (α term) of the solvent predominately decreases Φ_S for BID of **1b**, **1c** and **2.**

2.4. Solvent effect on the rate of chemiluminescent BID for oxyphenyl-substituted dioxetanes

The results in Table 1–4 (section 2.1) showed that the rate of BID was far more rapid in an aprotic polar solvent than in a protic solvent though it was particularly rapid in water. The features of this solvent-dependency of the rate expressed by k^{BID} are illustrated in Fig. 9. The k^{BID} for dioxetanes **1a**–**1c** and **2** was rather high in water, though it appeared to simply correlate with DN/AN of the

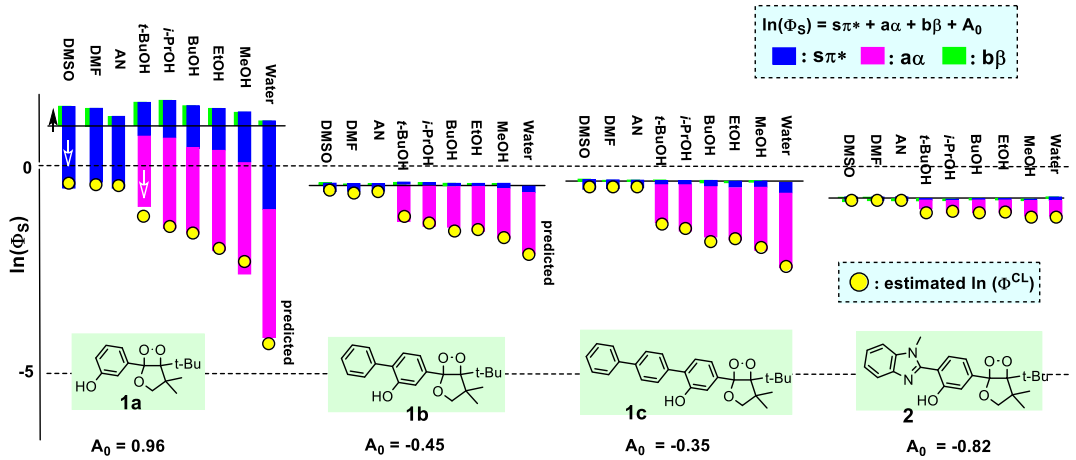


Fig. 8. Contributions of the π^*, α and β terms to the solvent effect on Φ_S for emitters **3a**–**3c** and **4** "The symbol ↑ means that the term contributes to increase Φ_S, while ↓ means that the term contributes to decrease Φ_S."

solvents, except water, as shown in Table 1–4 and Fig. 9. Thus, we carried out an LSER analysis of k^{BID} for dioxetanes **1b**, **1c** and **2**: an analysis was not performed for **1a**, since the k^{BID} values were measured at 25 °C in an aprotic polar solvent, but at 45 °C in a protic solvent.

The results of a multivariate analysis of the data in Table 2–4 were consistent with LSER as shown in eq. (14)–16:

$$\ln\left(k^{BID}\ for\ \mathbf{1b}\right) = 4.78\pi^* - 2.83\alpha + 0.40\beta - 6.44 \quad \left(R^2 = 0.978\right) \quad \text{(eq. 14)}$$

$$\ln\left(k^{BID}\ for\ \mathbf{1c}\right) = 3.55\pi^* - 3.36\alpha + 0.61\beta - 5.48 \quad \left(R^2 = 0.984\right) \quad \text{(eq. 15)}$$

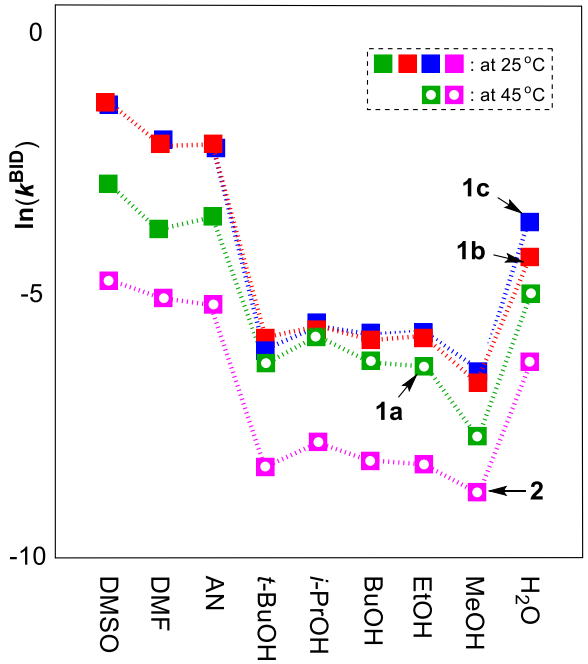


Fig. 9. Dependency of k^{BID} on the solvent for the chemiluminescent BID of dioxetanes **1a**–**1c** and **2**.

$$\ln\left(k^{BID}\ for\ \mathbf{2}\right) = 4.19\pi^* - 1.84\alpha + 0.33\beta - 9.06 \quad \left(R^2 = 0.966\right) \quad \text{(eq. 16)}$$

Equation (14)–16 for k^{BID} show a large positive coefficient for parameter π^*, in contrast to the cases of Φ^{CL}, Φ^{fl} and Φ_S (eq. (2)–13) and a large negative coefficient for parameter α. Thus, the LSER analysis suggested that BID of **1b, 1c**, and **2**, with respect to the rate, was disfavored in a solvent with a large HBD ability/Lewis-acidity (α term), and favored in a solvent with a large dipolarity/polarizability (π^* term): the HBA ability/Lewis-basicity (β term) of the solvent unexpectedly did not contribute much to BID: the coefficient for the β term was relatively small. The data of k^{BID} for **1a** were presumably consistent with the above suggestion based on LSER analysis for dioxetanes **1b**, **1c** and **2** (see Fig. 9 and ESI).

Based on eq. (14)–16, the contributions of the π^*, α and β terms to the solvent effect on k^{BID} are illustrated in Fig. 10, which explains how the solvents affect k^{BID} for BID of **1b**, **1c** and **2**:

i) Dipolarity/polarizability (π^* term) of the solvent contributes to increase k^{BID} while the HBD ability/Lewis-acidity (α term) of the solvent competitively acts to decrease k^{BID}. Thus, k^{BID} markedly decreases in alcohols in contrast to the change in aprotic polar solvents. However, a large π^* term prevents the marked decrease of k^{BID} in water.
ii) The contribution of the HBA ability/Lewis-basicity (β term) is far smaller than those of the π^* and α terms.

3. Conclusions

The TBD-mediated reactions of bicyclic dioxetanes bearing a 3-hydroxyphenyl **1a**, 2-hydroxybiphenyl-4-yl **1b**, 2-hydroxy-*p*-terphenyl-4-yl **1c**, and 4-(*N*-methylbenzimidazol-2yl)-3-hydroxyphenyl **2** were investigated to understand how the solvent affected chemiluminescent BID. The selected solvents were DMSO, DMF, AN (acetonitrile) as a representative aprotic polar solvent, *t*-BuOH (tertiary alcohol), *i*-PrOH (secondary alcohol), BuOH, EtOH, MeOH (primary alcohol) and water.

For the chemiluminescence spectra (represented by λ_{max}^{CL}) and rates of BID (represented by k^{BID}), we found that i) the λ_{max}^{CL} values varied in a range < 20 nm depending on the solvent system, though they showed a red-shift from an aprotic polar solvent to a protic solvent for dioxetanes **1a** (470 → 490 nm) and **1b** (480 → 497 nm) while they showed a blue-shift from a aprotic polar solvent to a

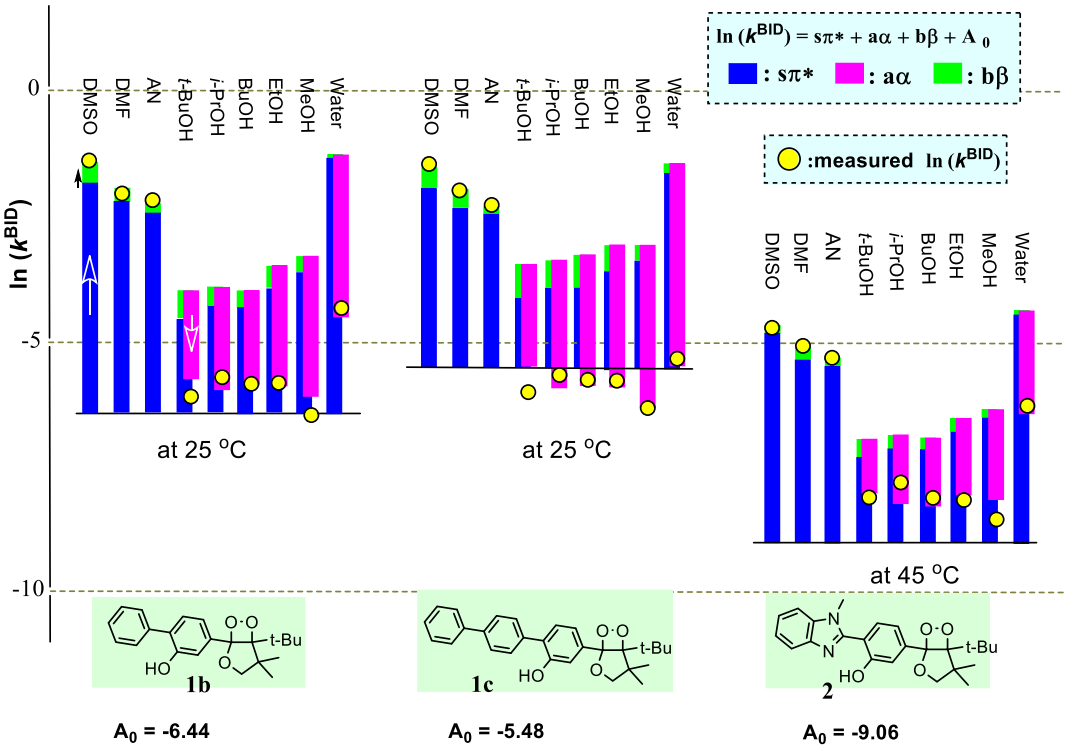


Fig. 10. Contributions of the π^*, α and β terms to the solvent effect on k^{BID} for dioxetanes **1b**, **1c**, and **2**. "The symbol ↑ means that the term contributes to increase k^{BID}, while ↓ means that the term contributes to decrease k^{BID}."

protic solvent for dioxetanes **1c** (508 → 488 nm) and **2** (485 → 480 nm), and ii) the rate of BID tended to decrease in a protic solvent except for water in comparison to in an aprotic polar solvent for all of the dioxetanes **1a**–**c** and **2**: k^{BID} decreased in the order DMSO > DMF ≥ AN > water > *i*-PrOH > BuOH ≥ *t*-BuOH > EtOH > MeOH. LSER analysis suggested that BID of oxyaryl-substituted dioxetanes, with respect to the reaction rate, was favored in a solvent with a large dipolarity/polarizability, and disfavored in a solvent with a large HBD ability/Lewis-acidity: the HBA ability/Lewis-basicity of the solvent unexpectedly did not contribute much to the rate of BID: the large k^{BID} in water is due to the high dipolarity/polarizability of water.

The chemiluminescence efficiency Φ^{CL} was found to be markedly affected by the solvent for BID of dioxetanes **1a**–**1c**, as follows. Φ^{CL} for **1a**–**1c** decreased in the order DMSO ≥ DMF > AN > *t*-BuOH > *i*-PrOH > BuOH > EtOH > MeOH » water: a similar trend was seen for **2**, but was far less sensitive to the solvent type. Φ^{CL} of **1a** was the most strongly affected by the solvent among the four dioxetanes investigated. The solvent-dependency for Φ^{CL} of **1a** showed a hierarchy that could be stratified into three classes: Φ^{CL} in an aprotic polar solvent » in alcohols » in water. The reactions for **1b**, **1c** and **2** appeared to show a similar hierarchy though not so obviously as for **1a**. An LSER analysis suggested that, for the solvent effect on Φ^{CL}, i) the hierarchy observed could be mainly attributed to the HBD ability/Lewis-acidity of the solvent, and ii) the noticeable drop of Φ^{CL} in water was most likely due to the fact that water has the largest dipolarity/polarizability and HBD ability/Lewis-acidity but the smallest HBA ability/Lewis-basicity among all of the solvents investigated.

Φ^{CL} is expressed as a product of $\Phi^{fl} \times \Phi_S$ for BID of dioxetanes. Both Φ^{fl} and Φ_S decreased in the order aprotic polar solvents ≥ (≤) *t*-BuOH > *i*-PrOH > BuOH > EtOH > MeOH > water for all of the four dioxetanes examined, though the former was more strongly affected by the solvent than the latter: for example, Φ^{fl} of **3a** (emitter for **1a**) in DMSO decreased to 1/140 in MeOH and 1/250 in water, while Φ_S of **1a** in DMSO decreased to 1/7 in MeOH and 1/55 in water. An LSER analysis suggested that the HBD ability/Lewis-acidity and dipolarity/polarizability of the solvent decreased Φ^{fl} while the HBA ability/Lewis-basicity competitively increased Φ^{fl}. On the other hand, Φ_S was suggested to be practically affected only by the HBD ability/Lewis-acidity of the solvent.

4. Experimental section

General. TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) and MTBD (methylated TBD) were purchased from commercial suppliers and used without further purification. DMSO, DMF, AN, EtOH and MeOH with spectroscopic grade, and *t*-BuOH with special grade, BuOH dehydrated, and *i*-PrOH with HPLC grade were purchased and used without further purification. Dioxetanes **1a**–**1c** and **2** and keto esters **5a**–**5c** and **6** were synthesized as described in our previous reports [17,33,36].

4.1. Measurement of chemiluminescence and time-course of the base-induced decomposition of dioxetanes; General Procedure: Chemiluminescence was measured using a Hamamatsu Photonics PMA-11 multi-channel detector equipped with constant temperature controller and stirrer.

4.1.1. *BID of **1a**, **1b** and **1c***Chemiluminescence reactions were carried out in all of the solvent systems (DMSO, DMF, AN, *t*-BuOH, *i*-PrOH, BuOH, EtOH, MeOH, and water), except **1a** in alcohols and water systems, as follows. A freshly prepared solution of TBD in a solvent (6.7×10^{-3} mol/L, 2.9 mL) was transferred to a quartz cell ($10 \times 10 \times 50$ mm) that was thermostated with stirring at 25 °C. After 3–5 min, a solution of dioxetane in AN (1.0×10^{-3} mol/L, 0.10 mL) was added by means of a pipettor, and measurement was started immediately. The time-course of the intensity of light emission was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with

that of an adamantylidene dioxetane, the chemiluminescence efficiency Φ^{CL} of which has been reported to be 0.29 and which was used here as a standard [42].

4.1.2. B*ID of **1a** in t*-BuOH, *i*-PrOH, BuOH, or EtOHSimilarly to the case in 4.1.1, measurement of chemiluminescence and time-course of the BID of **1a** were carried out, though concentrations of TBD and **1a** and reaction temperature were changed: a TBD solution (3.4×10^{-2} mol/L, 2.9 mL) and a solution of **1a** in AN (5.0×10^{-3} mol/L, 0.1 mL) were used at 45 °C.

4.1.3. BID *of **1a** in MeOH or water*Similarly to the case in 4.1.1, measurement of chemiluminescence and time-course of the BID of **1a** were carried out, though concentrations of TBD and **1a** and reaction temperature were changed: a TBD solution (6.7×10^{-2} mol/L, 2.9 mL) and a solution of **1a** in AN (1.0×10^{-2} mol/L, 0.1 mL) were used at 45 °C.

4.1.4. BID of 2¶. Similarly to the case in 4.1.1, measurement of chemiluminescence and time-course of the BID of **2** were carried out at 45 °C but not 25 °C.

*4.1. Measurement of fluorescence of authentic emitters **3a**–**3c** and **4**; general procedure*

Fluorescence spectra of authentic emitters **3a**–**3c** and **4** were measured by using a JASCO FP-6200 spectrometer and PMA-11 multi-channel detector, while absorption spectra of authentic emitters **3a**–**3c** and **4** were measured by using a JASCO V-660 spectrometer.

A freshly prepared solution of MTBD (6.9×10^{-3} mol/L, 2.9 mL) was transferred to a quartz cell ($10 \times 10 \times 50$ mm) and a solution of keto esters **5b-5c**, and **6** (1.0×10^{-3} mol/L, 0.1 mL) was added into a quartz cell, and was placed in the spectrometer.

For the case of keto ester **5a**, a solution of **5a** in AN (1.0×10^{-3} mol/L, 0.1 mL) was added to a freshly prepared solution of MTBD (6.9×10^{-3} mol/L, 2.9 mL) in DMSO, DMF or AN, while for the case of alcohols (*t*-BuOH, *i*-PrOH, BuOH, EtOH, MeOH) and water, a solution of **5a** in AN (1.0×10^{-2} mol/L, 0.1 mL) was added to a freshly prepared solution of MTBD (6.9×10^{-2} mol/L, 2.9 mL).

Electronic absorption spectra and fluorescence spectra of the thus-prepared authentic emitters **3a-3c**, and **4** were measured and their fluorescence efficiencies (Φ^{FL}) were estimated with quinine sulfate as a standard.

Declaration of competing interest

The authors declare that they haveno known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132147.

References

[1] A.P. Schaap, R.S. Handley, B.P. Giri, Tetrahedron Lett. 28 (1987) 935.
[2] A.P. Schaap, T.S. Chen, R.S. Handley, R. DeSilva, B.P. Giri, Tetrahedron Lett. 28 (1987) 1155.
[3] S. Beck, H. Köster, Anal. Chem. 62 (1990) 2258.
[4] W. Adam, D. Reihardt, C.R. Saha-Möller, Analyst 121 (1996) 1527.
[5] M.J. Matsumoto, Photochem. Photobiol., C, Photochem. Rev. 5 (2004) 27.
[6] F.A. Augusto, G.A. Souza, S.P. Souza Jr., M. Khalid, W.J. Baader, Photochem. Photobiol. 89 (2013) 1299.
[7] M. Vacher, I.F. Galván, B.W. Ding, S. Schramm, R. Berraud-Pache, P. Naumov, N. Ferré, Y.J. Liu, I. Navizet, D. Roca-Sanjuán, W.J. Baader, R. Lindh, Chem. Rev. 118 (2018) 6927.
[8] W. Adam, A.V. Trofimov, in: Z. Rappoport (Ed.), The Chemistry of Peroxides, vol. 2, Wiley, New York, NY, 2006, pp. 1171–1209.
[9] W.J. Baader, C.V. Stevani, E.L. Bastos, in: Z. Rappoport (Ed.), The Chemistry of Peroxides, vol. 2, Wiley, NewYork, NY, 2006, pp. 1211–1278.
[10] I. Bronstein, B. Edwards, J.C. Voyta, J. Biolumin. Chemilumin. 4 (1989) 99.
[11] A.P. Schaap, H. Akhavan, L.J. Romano, J. Clin. Chem. 35 (1989) 1863.
[12] W. Adam, I. Bronstein, A.V. Trofimov, R.F. Vasil'ev, J. Am. Chem. Soc. 121 (1999) 958.
[13] M. Yamada, K. Kitaoka, M. Matsumoto, N. Watanabe, in: A. Tsuji, M. Matsumoto, M. Maeda, L.J. Kricka, P.E. Stanley (Eds.), Bioluminescence and Chemiluminescence, World Scientific, Singapore, 2004, pp. 487–490.
[14] A.V. Trofimov, R.F. Vasil'ev, K. Mielke, W. Adam, Photochem. Photobiol. 62 (1995) 35.
[15] W. Adam, I. Bronstein, B. Edwards, T. Engel, D. Reinhardt, F.W. Schneider, A.V. Trofimov, R.F. Vasil'ev, J. Am. Chem. Soc. 118 (1996) 10400.
[16] M. Matsumoto, N. Watanabe, N.C. Kasuga, F. Hamada, K. Tadokoro, Tetrahedron Lett. 38 (1997) 2863.
[17] M. Matsumoto, Y. Mizoguchi, T. Motoyama, N. Watanabe, Tetrahedron Lett. 42 (2001) 8869.
[18] W. Adam, M. Matsumoto, A.V. Trofimov, J. Am. Chem. Soc. 122 (2000) 8631.
[19] W. Adam, M. Matsumoto, A.V. Trofimov, J. Org. Chem. 65 (2000) 2078.
[20] N. Hananya, A.E. Boock, C.R. Bauer, R. Satchi-Fainaro, D. Shabat, J. Am. Chem. Soc. 138 (2016) 13438.
[21] N. Watanabe, H. Kino, S. Watanabe, H.K. Ijuin, M. Yamada, M. Matsumoto, Tetrahedron 68 (2012) 6079.
[22] M. Matsumoto, T. Sakuma, N. Watanabe, Tetrahedron Lett. 43 (2002) 8955.
[23] M. Matsumoto, T. Akimoto, Y. Matsumoto, N. Watanabe, Tetrahedron Lett. 46 (2005) 6075.
[24] M. Tanimura, N. Watanabe, H.K. Ijuin, M. Matsumoto, J. Org. Chem. 75 (2010) 3678.
[25] M. Tanimura, N. Watanabe, H.K. Ijuin, M. Matsumoto, J. Org. Chem. 76 (2011) 902.
[26] J. Kocčí, V. Grandclaude, M. Massonneau, J.A. Richard, A. Romieu, P.Y. Renard, Chem. Commun. 47 (2011) 6713.
[27] O. Green, T. Eilon, N. Hananya, S. Gutkin, C.R. Bauer, D. Shabat, ACS Cent. Sci. 3 (2017) 349.
[28] N. Hananya, D. Shabat, Angew. Chem. Int. Ed. 56 (2017) 16454.
[29] S. Gnaim, O. Green, D. Shabat, Chem. Commun. 54 (2018) 2073.
[30] N. Hananya, O. Press, A. Das, A. Scomparin, R. Satchi-Fainaro, I. Sagai, D. Shabat, Chem. Eur J. 25 (2019) 14679.
[31] N. Hananya, J.P. Reid, O. Green, M.S. Sigman, D. Shabat, Chem. Sci. 10 (2019) 1380.
[32] W. Adam, I. Bronstein, A.V. Trofimov, J. Phys. Chem. 102 (1998) 5406.
[33] N. Watanabe, H. Takatsuka, H.K. Ijuin, M. Matsumoto, Tetrahedron 76 (2020) 131203.
[34] M.J. Kamlet, J.L.M. Abboud, R.W. Taft, in: R. Taft (Ed.), Progress in Physical Organic Chemistry, vol. 13, Wiley, New York, 1981, pp. 485–630.
[35] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. 48 (1983) 2877.
[36] H. Hagiwara, N. Watanabe, H.K. Ijuin, M. Yamada, M. Matsumoto, Heterocycles 87 (2013) 65.
[37] I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito, I.A. Koppel, J. Org. Chem. 70 (2005) 1019.
[38] R.C. Pratt, B.G.G. Lohmeijer, D.A. Long, R.M. Waymouh, J.L. Hedrick, J. Am. Chem. Soc. 128 (2006) 4556.
[39] E.I. Rõõm, A. Kütt, I. Kaljurand, I. Koppel, I. Leito, I.A. Koppel, M. Mishima, K. Goto, Y. Miyahara, Chem. Eur J. 13 (2007) 7631.
[40] N. Watanabe, A. Wakatsuki, H.K. Ijuin, Y. Kabe, M. Matsumoto, Tetrahedron Lett. 59 (2018) 971.
[41] Φ^{CL} was estimated based on the value 0.29 for the chemiluminescent decomposition of 3-adamantylidene-4-methoxy-4-(3-oxidophenyl)-1,2-dioxetane in a TBAF/DMSO system [42].
[42] A.V. Trofimov, K. Mielke, R.F. Vasil'ev, W. Adam, Photochem. Photobiol. 63 (1996) 463.
[43] L. Tu, Y. Wang, Y. Yang, B.H. Bakker, X. Kong, A.M. Brouwer, W.J. Buma, H. Zhang, Phys. Chem. Chem. Phys. 12 (2010) 6789.
[44] N. Watanabe, A. Oguri, M. Horikoshi, H. Takatsuka, H.K. Ijuin, M. Matsumoto, Tetrahedron Lett. 55 (2014) 1644.
[45] C. Sabot, K.A. Kumar, S. Meunier, C. Mioskowski, Tetrahedron Lett. 48 (2007) 3863.