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Chemiluminescence in anisotropic microenvironment: splitting of chemiluminescence efficiency for charge-transfer-induced decomposition of optically active bicyclic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-4-yl moiety under chiral recognition

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Abstract—Four optical isomers of dioxetane **2** bearing a 2-hydroxy-1,1′-binaphthyl-4-yl moiety decomposed with accompanying emission of light on treatment with three base systems. The chemiluminescence efficiencies of all isomers were practically the same for tetrabutylammonium fluoride (TBAF) in DMSO system, whereas they split into two diastereomer-groups for 18-crown-6 ether complex of *t*-BuOK in benzene–THF system. For the base system using *t*-BuOK complex of optically active crown ether, (*Ra*,*Ra*)-**7** or (*Sa*,*Sa*)-**7**, the chemiluminescence efficiencies split further into four. The shape of chemiluminescence spectrum, maximum wavelength, and the rate of decomposition were also different between each of the four stereoisomers.
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It has very recently been reported that optically active diaoxetanes **1** bearing a 2-hydroxy-1,1′-binaphthyl-5-yl group display intramolecular charge-transfer-induced chemiluminescence (CTICL)[1–4] in the coordination sphere of an optically active crown ether complex, where the features of coordination based on the chiral recognition were reflected in their spectra of chemiluminescence.[5] In the course of our further investigation of CTICL in optically anisotropic environment, we synthesized four optically active dioxetanes **2** bearing a 2-hydroxy-1,1′-binaphthyl-4-yl group, in the expectation that the dioxetane ring of **2** would be affected sterically much more by the coordination sphere than the case of **1**, since it lies near the oxido anion to be coordinated. Thus, we found that chemiluminescent decomposition of **2** caused an unusual splitting of chemiluminescence efficiency under chiral recognition as well as under diastereomeric recognition, in addition to the spectral change under chiral recognition (Fig. 1).

Four optical isomers of dioxetane **2** were synthesized by the singlet oxygenation of dihydrofurans substituted with an atropisomeric 2-hydroxy-1,1′-binaphthyl-4-yl group, (*Ra*)-**3** and (*Sa*)-**3**, which were prepared through resolution of an optically active (1*S*)-(+)-camphorsulfonate **4**: X-ray single crystallographic analysis of diastereomer (*Sa*,1*S*)-**4** was successfully achieved as illustrated in Figure 2.[6] Thus, (*Ra*)-**3** afforded a diastereomeric mixture of dioxetanes, (*Ra*,1*R*,5*R*)-**2** and (*Ra*,1*S*,5*S*)-**2** while (*Sa*)-**3** gave a mixture of (*Sa*,1*S*,5*S*)-**2** and (*Sa*,1*R*,5*R*)-**2** exclusively. Usual column chromatography on silica gel was successful for the isolation of these isomers to give (*Ra*,1*R*,5*R*)-**2** ($[\alpha]_D^{25}$ −26.1 in 1,4-dioxane), (*Ra*,1*S*,5*S*)-**2** ($[\alpha]_D^{25}$ 139.2 in 1,4-dioxane), (*Sa*,1*S*,5*S*)-**2** ($[\alpha]_D^{25}$ 26.2 in 1,4-dioxane), and (*Sa*,1*R*,5*R*)-**2** ($[\alpha]_D^{25}$ −140.5 in 1,4-dioxane) in 35–50% yields. The structures of these dioxetanes were determined by ^{1}H NMR, ^{13}C NMR, IR, Mass, and HR mass spectral analysis.[7,8] Stereochemistry of these optically active dioxetanes was determined on the basis of X-ray single crystallographic analysis of (*Ra*,1*S*,5*S*)-**2**, the ORTEP view of which is illustrated in Figure 2.[6] The thus-obtained optically active dioxetanes **2** were quite stable thermally in the dark, though they decomposed into optically active keto esters **5** exclusively in hot xylene; both (*Ra*,1*R*,5*R*)-**2** and (*Ra*,1*S*,5*S*)-**2**
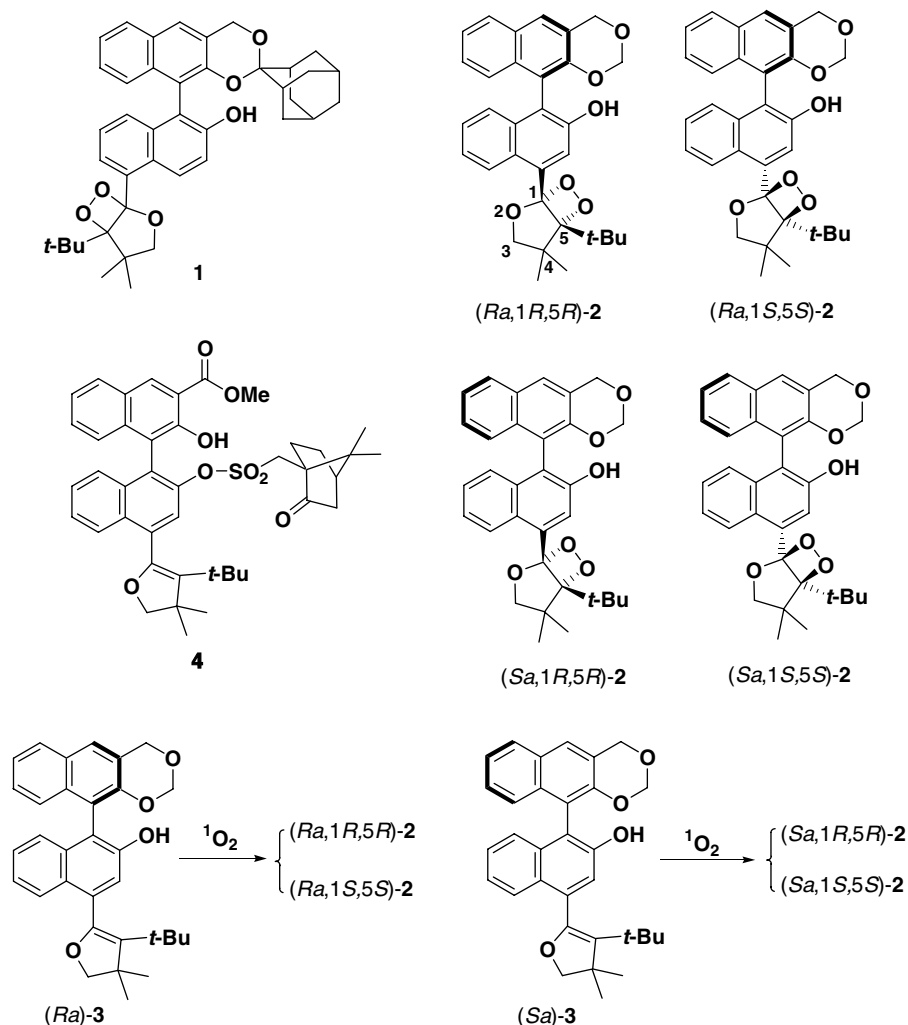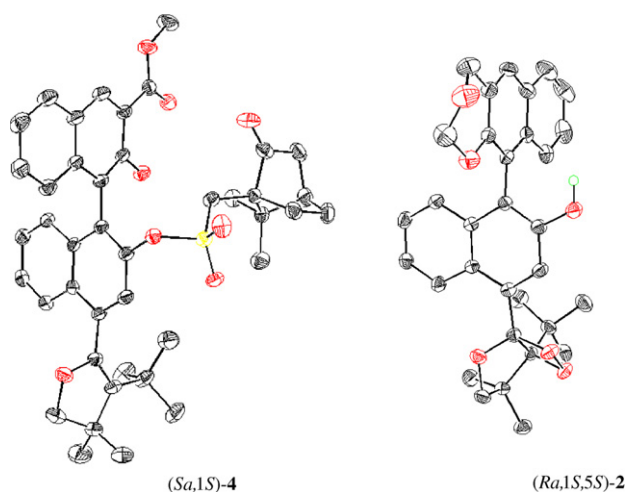
Figure 1.

Figure 2. ORTEP views of (*Sa*,1*S*)-**4** and (*Ra*,1*S*,5*S*)-**2**.

yielded (*Ra*)-**5**, while both (*Sa*,1*S*,5*S*)-**2** and (*Sa*,1*R*,5*R*)-**2** afforded (*Sa*)-**5** (Scheme 1).

First of all, CTICL decomposition of four optical isomers of dioxetane **2** was examined in a completely homo-geneous system. When dioxetane (*Ra*,1*R*,5*R*)-**2** was treated with a large excess of tetrabutylammonium fluo-ride (TBAF) in DMSO at 25 °C, it decomposed rapidly into a naphthoxide anion of keto ester (*Ra*)-**6** to afford yellow light with maximum wavelength $\lambda_{max}^{CTICL} = 525$ nm, chemiluminescence efficiency $\Phi^{CTICL} = 1.9 \times 10^{-2}$, and CTICL-decomposition rate $k^{CTICL} = 1.7 \times 10^{-2}\,s^{-1}$.[9,10] Similar treatment of its enantiomeric dioxe-tane (*Sa*,1*S*,5*S*)-**2** with TBAF also gave light with the same chemiluminescence properties as those for (*Ra*,1*R*, 5*R*)-**2**. On the other hand, their *meso*-diastereomers, (*Ra*,1*S*,5*S*)-**2** and (*Sa*,1*R*,5*R*)-**2**, also afforded yellow light ($\lambda_{max}^{CTICL} = 525$ nm) with Φ^{CTICL}s the same substantially as in the case of *dl*-isomers, though k^{CTICL}s were ca 1/2 of those for *dl*-isomers, (*Ra*,1*R*,5*R*)-**2** and (*Sa*,1*S*,5*S*)-**2**. These results are summarized in Table 1.

Next, we examined CTICL of dioxetanes **2** by the use of 18-crown-6 ether complex with *t*-BuOK, [K ⊂ (18C6)]⁺*t*-BuO⁻, in benzene (PhH)–tetrahydrofuran (THF) (1:1), which provided a sterically anisotropic though not optically active microenvironment on the coordination of **2**. When stereoisomeric dioxetanes **2** were individually treated with a large excess of
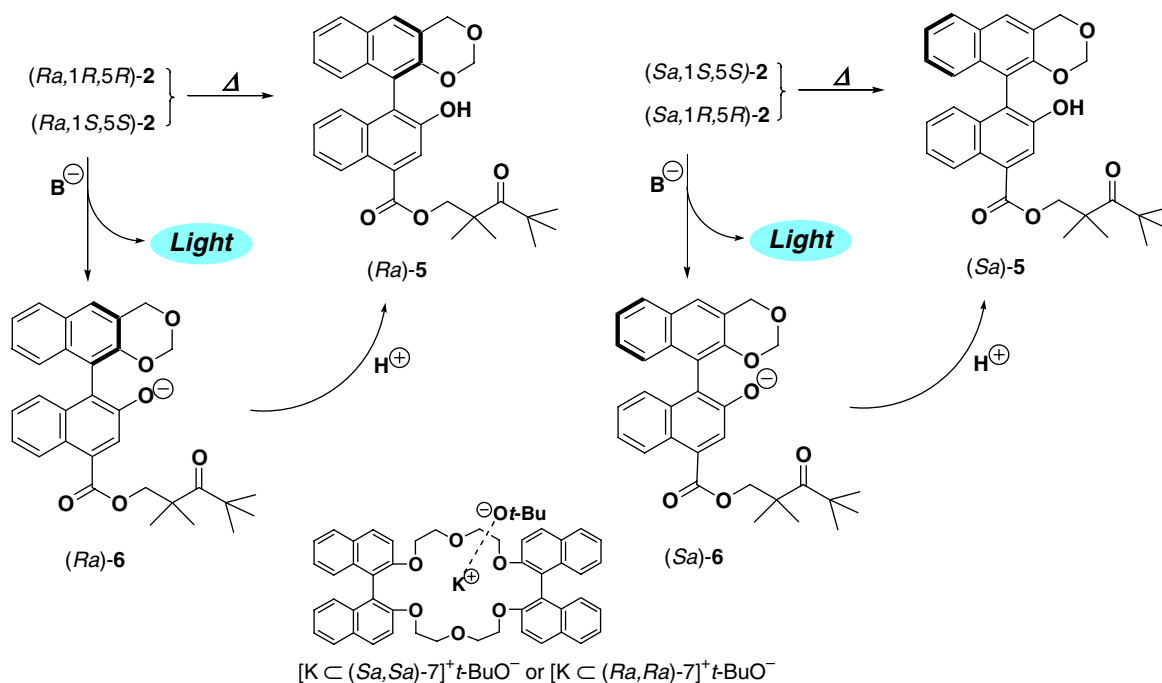
Scheme 1.

Table 1. Chemiluminescence properties of stereoisomeric dioxetanes **2**

Triggering system		dl-Type		meso-Type	
		$(Ra,1R,5R)$-**2**	$(Sa,1S,5S)$-**2**	$(Ra,1S,5S)$-**2**	$(Sa,1R,5R)$-**2**
TBAF[a]	λ_{max}^{CTICL}/nm	525	525	525	525
	Φ^{CTICL} [d]	1.9×10^{-2}	2.0×10^{-2}	1.8×10^{-2}	1.9×10^{-2}
	k^{CTICL}/s^{-1}	1.7×10^{-2}	1.7×10^{-2}	7.8×10^{-3}	7.6×10^{-3}
$[K \subset (18C6)]^+ t$-BuO^{-}[b]	λ_{max}^{CTICL}/nm	533	533	533	533
	Φ^{CTICL} [d]	2.6×10^{-3}	2.6×10^{-3}	1.5×10^{-3}	1.5×10^{-3}
	k^{CTICL}/s^{-1}	1.4×10^{-3}	1.4×10^{-3}	1.5×10^{-3}	1.6×10^{-3}
$[K \subset (Ra,Ra)$-**7**$]^+ t$-BuO^{-}[c]	λ_{max}^{CTICL}/nm	552	556	551	542
	Φ^{CTICL} [d]	5.0×10^{-3}	1.5×10^{-2}	7.7×10^{-3}	2.6×10^{-3}
	k^{CTICL}/s^{-1}	1.2×10^{-4}	4.9×10^{-4}	1.3×10^{-4}	1.2×10^{-4}
$[K \subset (Sa,Sa)$-**7**$]^+ t$-BuO^{-}[c]	λ_{max}^{CTICL}/nm	556	552	542	551
	Φ^{CTICL} [d]	1.4×10^{-2}	5.5×10^{-3}	2.6×10^{-3}	7.7×10^{-3}
	k^{CTICL}/s^{-1}	4.6×10^{-4}	1.1×10^{-4}	1.1×10^{-4}	1.4×10^{-4}

[a] A solution of dioxetane **2** in DMSO (1.0×10^{-5} mol dm^{-3}, 1 mL) was added to a solution of TBAF in DMSO (1.0×10^{-2} mol dm^{-3}, 2 mL) at 25 °C.

[b] A solution of dioxetane **2** in PhH–THF (1:1) (1.0×10^{-4} mol dm^{-3}, 1 mL) was added to a solution of $[K \subset (18C6)]^+ t$-BuO$^-$ in PhH–THF (1:1) (1.0×10^{-1} mol dm^{-3}, 2 mL) at 25 °C.

[c] A solution of dioxetane **2** in PhH–THF (1:1) (1.0×10^{-4} mol dm^{-3}, 1 mL) was added to a solution of $[K \subset (7)]^+ t$-BuO$^-$ in PhH–THF (1:1) (1.0×10^{-2} mol dm^{-3}, 2 mL) at 25 °C.

[d] Relative quantum yields based on the value for 3-adamatylidene-3-methoxy-4-(3-siloxyphenyl)-1,2-dioxetane (Ref. 10).

$[K \subset (18C6)]^+ t$-BuO$^-$ at 25 °C, they displayed chemiluminescence, the properties of which are summarized in Table 1. The results in Table 1 reveal that (a) all stereoisomers **2** afforded light with the same λ_{max}^{CTICL} (533 nm), which was a little longer than that for TBAF in DMSO, and (b) Φ_s^{CTICL} split into two diastereomer groups, namely, dl-type and meso-type.

Finally, we examined CTICL decomposition of stereoisomeric dioxetanes **2** by the use of a complex of optically active crown ethers, (Ra,Ra)-**7** or (Sa,Sa)-**7**,[11,12]

with t-BuOK in PhH–THF (1:1). When dioxetane $(Ra,1R,5R)$-**2** was treated with $[K \subset (Ra,Ra)$-**7**$]^+ t$-BuO$^-$ at 25 °C, it displayed chemiluminescence with $\lambda_{max}^{CTICL} = 552$ nm, $\Phi^{CTICL} = 5.0 \times 10^{-3}$, and $k^{CTICL} = 1.2 \times 10^{-4}$ s^{-1}, the spectrum of which is illustrated in Figure 3. Similar treatment of another enantiomer, $(Sa,1S,5S)$-**2**, gave light with $\lambda_{max}^{CTICL} = 556$ nm, $\Phi^{CTICL} = 1.5 \times 10^{-2}$, and $k^{CTICL} = 4.9 \times 10^{-4}$ s^{-1} (Table 1, Fig. 3). These results show that shape of CTICL spectrum and λ_{max}^{CTICL} were somewhat different between these enantiomers, whereas distinctly different were Φ^{CTICL} and k^{CTICL}.
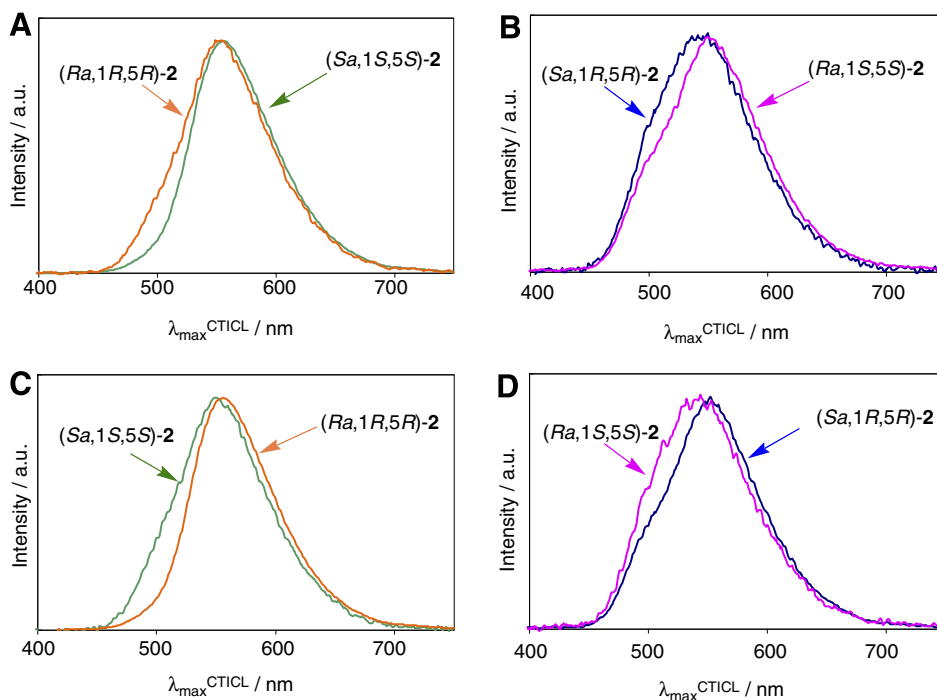
Figure 3. Chemiluminescence spectra for the decomposition of optically active dioxetanes **2** induced by a complex of optically active crown ether with *t*-BuOK. (A, B): $[K \subset (Ra,Ra)\text{-}7]^+ t\text{-BuO}^-$ in PhH–THF (1:1) (C, D): $[K \subset (Sa,Sa)\text{-}7]^+ t\text{-BuO}^-$ in PhH–THF (1:1).

Differences in Φ^{CTICL}, k^{CTICL}, λ_{max}^{CTICL}, and the shape of the spectrum were observed not only between enantiomers but also between each of four stereoisomers **2** and the others, as shown in Table 1 and Figure 3. When a complex of another enantiomeric crown ether, $[K \subset (Sa,Sa)\text{-}7]^+ t\text{-BuO}^-$, was used for CTICL decomposition of **2**, each of the four stereoisomers gave light with properties, which exchanged completely reciprocally with the case using $[K \subset (Ra,Ra)\text{-}7]^+ t\text{-BuO}^-$, as shown in Table 1 and Figure 3.

Among the changes in chemiluminescence properties disclosed, the change in chemiluminescence efficiency Φ^{CTICL} was unprecedented and was the most noticeable phenomenon found in this work. Figure 4 illustrates the whole feature of change in Φ^{CTICL} upon treatment of four stereoisomers **2** with TBAF in DMSO → $[K \subset (18C6)]^+ t\text{-BuO}^-$ in PhH–THF → $[K \subset (Ra,Ra)\text{-}7]^+ t\text{-BuO}^-$ and $[K \subset (Sa,Sa)\text{-}7]^+ t\text{-BuO}^-$ in PhH–THF. First, Φ_s^{CTICL} were substantially the same among four stereoisomers **2** in TBAF in DMSO as a completely homogeneous system. Next, Φ_s^{CTICL} split into two diastereomer groups, *meso*-type and *dl*-type, as the triggering system changed to a coordination system, $[K \subset (18C6)]^+ t\text{-BuO}^-$ in PhH–THF. Thirdly, Φ_s^{CTICL} for two diastereomer groups split further into four individuals, when an optically active crown ether complex $[K \subset (Ra,Ra)\text{-}7]^+ t\text{-BuO}^-$ was used. Finally, these four individuals were exchanged reciprocally between enantiomers in the system of $[K \subset (Sa,Sa)\text{-}7]^+ t\text{-BuO}^-$. The difference in Φ^{CTICL} was significantly large and there was ca. six times gap between the highest Φ^{CTICL} and the lowest one.

All spent reaction mixtures of four stereoisomeric dioxetanes **2** for the TBAF in DMSO system afforded
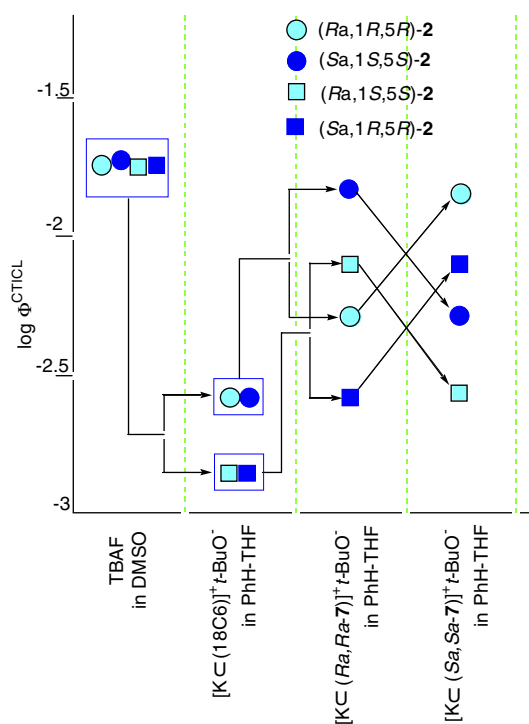

Figure 4.

the corresponding ketoester (*Ra*)-**5** or (*Sa*)-**5** selectively after neutralization, and they displayed fluorescence, the maximum wavelengths (λ_{max}^{fl}) of which coincided with λ_{max}^{CTICL} of chemiluminescence from dioxetanes **2**. The fluorescence spectra of authentic ketoesters, (*Ra*)-**6** and (*Sa*)-**6**, generated from (*Ra*)-**5** and (*Sa*)-**5**, coincided also with the chemiluminescence spectra of dioxetanes **2**
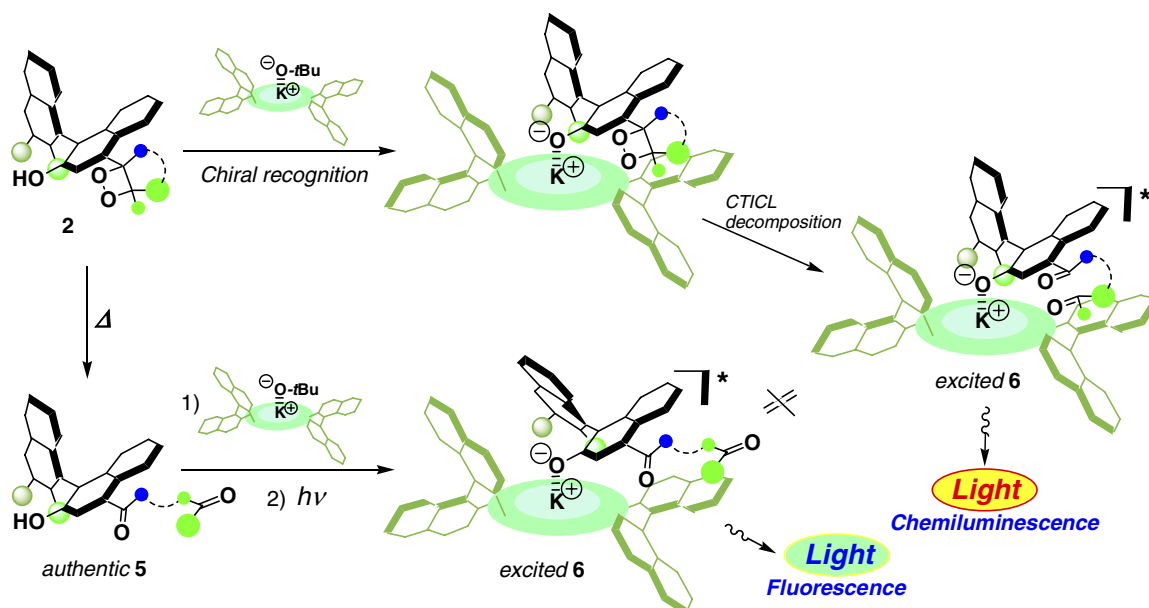
Figure 5.

for TBAF in DMSO system. These results exhibit that the emitter produced from **2** was undoubtedly the naphthoxide anion of ketoester (*Ra*)-**6** or (*Sa*)-**6**. Thus, singlet chemiexcitation efficiencies (Φ_s) were estimated to be 0.20–0.23 for CTICL of **2** in the TBAF in DMSO system. The spent reaction mixtures of dioxetanes **2** also gave selectively the corresponding ketoester (*Ra*)-**5** or (*Sa*)-**5**, after neutralization, for both [K ⊂ (18C6)]$^+$-*t*-BuO$^-$ in PhH–THF system and [K ⊂ **7**]$^+$*t*-BuO$^-$ in PhH–THF system. Therefore, the naphthoxide anion of ketoester **6** would be also the emitter for CTICL of **2** in the coordination sphere of the crown ether complex. However, spent reaction mixtures in these crown ether systems displayed fluorescence, λ_{max}^{fl} of which was far shorter than λ_{max}^{CTICL} of chemiluminescence for the same base systems: $\lambda_{max}^{fl} = 493$ nm for [K ⊂ (18C6)]$^+$*t*-BuO$^-$ in PhH–THF, while 501–508 nm for [K ⊂ **7**]$^+$*t*-BuO$^-$ in PhH–THF.

The change of the dihedral angle around an axis joining two aryl groups should cause the change of the fluorescence spectrum for the biaryl-type molecule.[13] According to this idea, the significant discrepancy between λ_{max}^{CTICL} of dioxetane and λ_{max}^{fl} of the authentic emitter suggests that the excited emitter produced from **2** by CTICL decomposition would lie in a conformation different from that of the authentic naphthoxide anion of **6** in the coordination sphere. That is to say, dioxetane **2** in the coordination sphere decomposes into excited ketoester **6**, the structure of which is presumably transient one that reflects the initial steric interaction of crown ether with both a naphthyl group and dioxetane ring attached to the oxidonaphthyl group coordinating to the central potassium ion (Fig. 5).

As described already, the split of Φ^{CTICL} correlates completely with the stereochemistry of dioxetanes **2**. This phenomenon is quite important from the viewpoint of the chemiexcitation mechanism of CTICL, which has been argued continuously. The results for CTICL induced by [K ⊂ (18C6)]$^+$*t*-BuO$^-$ reveal intriguing information regarding the features of the split of Φ^{CTICL}. Since all stereoisomeric dioxetanes **2** display chemiluminescence with the same λ_{max}^{CTICL} in the [K ⊂ (18C6)]$^+$*t*-BuO$^-$ system, they should produce, as emitter, excited naphthoxide anion of **6** with the same or at least similar conformation to that of the others except for optical isomerism. Therefore, the difference of splitting in Φ^{CTICL} between diastereomers, namely, *dl*- and *meso*-type **2**, is presumably attributed to the difference in singlet chemiexcitation efficiencies (Φ_s) between the diastereomers, since Φ_s^{fl} of emitters are the same with each other. This idea leads to a suggestion that change of the dihedral angle between the oxidonaphthyl ring and the dioxetane ring rather than that of binaphthyl may be important to control chemiexcitation efficiency. The conformational change around the oxidonaphthyl-dioxetane moiety should occur under the chiral recognition. The suggestion relates probably also to the proposal that the dihedral angle between an aromatic electron donor and the dioxetane ring influences significantly the rate of decomposition of CTICL-active dioxetanes.[3,4,14]

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6. Crystal data for compound (*Ra*,1*S*,5*S*)-**2**: $C_{32}H_{32}O_6 \cdot C_4H_8O$ (M_r = 584.71), colorless platelet, $0.30 \times 0.20 \times 0.15$ mm, orthorhombic, space group $P2_12_12_1$ (#19), a = 9.179(4) Å, b = 12.327(13) Å, c = 26.69(1) Å, V = 3020.3(38) Å^3, Z = 4, ρ_{calcd} = 1.286 g cm^{-3}, T = 150 K, $F(000)$ = 1248.00, reflections collected/unique 32349/6844 (R_{int} = 0.043), μ(Mo Kα) = 0.88 cm^{-1}. Final R indices $R1$ = 0.067 [$I > 2\sigma(I)$], $wR2$ = 0.196 (all data), GOF on F^2 = 1.005, and residual electron density 1.34/ − 0.84 e Å^{-3} CCDC deposition number: 618571.
Crystal data for compound (*Sa*,1*S*)-**4**: $C_{42}H_{46}O_8S$ (M_r = 710.88), colorless block, $0.35 \times 0.30 \times 0.20$ mm, orthorhombic, space group $P2_12_12_1$ (#19), a = 11.211(6) Å, b = 17.95(2) Å, c = 18.618(10) Å, V = 3745.8(49) Å^3, Z = 4, ρ_{calcd} = 1.260 g cm^{-3}, T = 150 K, $F(000)$ = 1512.00, reflections collected/unique 40645/8532 (R_{int} = 0.044), μ(Mo Kα) = 1.39 cm^{-1}. Final R indices $R1$ = 0.049 [$I > 2\sigma(I)$], $wR2$ = 0.124 (all data), GOF on F^2 = 1.014, and residual electron density 0.48/−0.48 e Å^{-3}. CCDC deposition number: 618572. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223 336 033; or deposit@ccdc.cam.au.uk).

7. Selected data for (*Ra*,1*R*,5*R*)-**2**: ^{1}H NMR (500 MHz, CDCl$_3$): δ_H 1.03 (s, 9H), 1.33 (s, 3H), 1.68 (s, 3H), 4.11 (d, J = 8.5 Hz, 1H), 4.74 (d, J = 8.5 Hz, 1H), 4.92 (s, 1H), 5.19 (q$_{AB}$, J = 6.0 Hz, 2H), 5.21 (s, 2H), 7.14 (d, J = 8.2 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.22 (dd with fine coupling, J = 8.2 and 6.9 Hz, 1H), 7.30 (dd, J = 8.2 and 6.9 Hz, 1H), 7.33 (dd with fine coupling, J = 8.7 and 6.9 Hz, 1H), 7.39 (dd, J = 8.2 and 6.9 Hz, 1H), 7.68 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 8.12 (m, 1H), 8.60 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 20.0, 26.2, 27.0, 36.9, 45.7, 66.8, 80.7, 91.9, 106.1, 114.5, 116.6, 117.2, 121.8, 122.5, 123.3, 124.5, 124.7, 125.6, 125.7, 126.2, 126.5, 127.0, 127.2, 128.0, 129.0, 132.7, 133.5, 134.7, 149.5, 150.2 ppm. Selected data for (*Ra*,1*S*,5*S*)-**2**: ^{1}H NMR (500 MHz, CDCl$_3$): δ_H 1.03 (s, 9H), 1.34 (s, 3H), 1.69 (s, 3H), 4.12 (d, J = 8.1 Hz, 1H), 4.75 (d, J = 8.1 Hz, 1H), 4.91 (s, 1H), 5.23 (s, 2H), 5.26 (q$_{AB}$, J = 5.7 Hz, 2H), 7.06 (d, J = 8.2 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.20–7.26 (m, 2H), 7.33 (dd with fine coupling, J = 8.7 and 6.7 Hz, 1H), 7.36 (dd with fine coupling, J = 8.2 and 6.7 Hz, 1H), 7.68 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 8.11 (m, 1H), 8.57 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 20.1, 26.3, 27.0, 37.0, 45.7, 66.9, 80.7, 92.0, 106.2, 114.6, 115.6, 116.7, 121.7, 122.5, 123.3, 124.8, 124.9, 125.7, 125.7, 126.2, 126.5, 126.9, 127.1, 127.8, 129.1, 132.9, 133.6, 134.7, 149.4, 150.2 ppm.

8. Quantitative analysis of isomeric dihydrofurans, (*Ra*)-**3** and (*Sa*)-**3**, was effectively attained by means of HPLC with chiral column (CHIRALCEL OP(+); solvent, MeOH; temp 33 °C) to estimate that optical purities were 98.8% ee for (*Ra*)-**3**, and 100% ee for (*Sa*)-**3**. However, the HPLC analysis was unsuccessful for determining the optical purities of four isomeric dioxetanes **2** at present. Therefore, optical purities were estimated tentatively to be 98.8% ee for (*Ra*,1*R*,5*R*)-**2** and (*Ra*,1*S*,5*S*)-**2**, and 100% ee for (*Sa*,1*R*,5*R*)-**2** and (*Sa*,1*S*,5*S*)-**2**, since the separation of diastereomers were successfully accomplished.

9. Chemiluminescent efficiencies were based on the value for 3-(3-*tert*-butyldimethylsiloxy)-3-methoxy-4-(2′-spiroadamantane)-1,2-dioxetane (Φ^{CTICL} = 0.29).[10]

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