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Color modulation for intramolecular charge-transfer-induced chemiluminescence of bicyclic dioxetanes bearing a 3-hydroxy-5-naphthylphenyl moiety in the coordination sphere

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Abstract—Bicyclic dioxetanes **2a**, **2b**, and **3**, bearing a 3-hydroxy-5-naphthylphenyl moiety underwent charge-transfer-induced decomposition with accompanying emission of light, the color of which changed from red to blue responding to a complex of crown ether with potassium *t*-butoxide used as a base. Furthermore, they afforded unusual chemiluminescence, the spectra of which displayed two peaks in some cases. It was observed for chemiluminescences in the coordination sphere with crown ether that their spectra did not coincide with the spectra of authentic emitters.

Dioxetanes substituted with an aryloxide anion undergo intramolecular charge-transfer (CT)-induced decomposition with accompanying emission of light, which ranges in color from violet to crimson depending on the oxidoaryl group.[1–3] However, there has been little known of chemiluminescent substrates that change the color of emission responding to the microenvironment except for dioxetane **1** bearing a 3-(anthracen-9-yl)-5-hydroxyphenyl moiety.[4] Thus, we synthesized here dioxetanes **2a**, **2b** and **3** bearing a 3-hydroxyphenyl moiety substituted with a rather small naphthalen-1-yl or naphthalen-2-yl group, and found that these dioxetanes displayed base-induced chemiluminescence, the spectra of which varied more intensively than the case of **1**, and exhibited two peaks in some cases; such phenomenon is presumably unprecedented for CTICL (CT-induced chemiluminescence) of dioxetanes (Fig. 1).

Sensitized photooxygenation of dihydrofurans, **4a**, **4b**, and **5**, in dichloromethane at 0 °C afforded exclusively the corresponding dioxetanes, **2a**, **2b**, and **3**, the structures of which were determined by ^{1}H NMR, ^{13}C NMR, IR, and mass spectral analysis.[5] Dioxetanes, **2a**, **2b**, and **3**, were quite stable thermally, though they decomposed exclusively into the corresponding keto esters **6a**, **6b**, and **7** on heating in xylene (Fig. 1).

When dioxetane **2a** was treated with a large excess of TBAF in DMSO at 25 °C, **2a** decomposed rapidly to afford orange light (maximum wavelength: $\lambda_{\max}^{\mathrm{CTICL}} = 582$ nm, chemiluminescent efficiency: $\Phi^{\mathrm{CTICL}} = 2.7 \times 10^{-3}$, pseudo-first order rate constant: $k^{\mathrm{CTICL}} = 1.1\ \mathrm{s}^{-1}$).[6,7] The spent reaction mixture afforded keto ester **6a** in high yield after neutralization. The fluorescence spectrum of **8a** generated from authentic **6a** coincided with the chemiluminescent spectrum of **2a** in TBAF/DMSO. These results suggest strongly that CTICL decomposition of **2a** produced excited keto ester **8a** as an emitter. On the other hand, **2a** displayed chemiluminescent spectrum with $\lambda_{\max}^{\mathrm{CTICL}}$ (615 nm) longer than the case of TBAF/DMSO on treatment with tetrabutylammonium *t*-butoxide (TBA^{+}*t*-BuO^{-}) in benzene (PhH). Such solvatochromism has not been reported for dioxetane **1**,[4] though observed for parent dioxetane **10** to some extent, as shown in Table 1.

Next, CTICL decomposition of **2a** was carried out by the use of a potassium *t*-butoxide complex of a crown ether, [K ⊂ (crown ether)]$^{+}$*t*-BuO^{-}, in PhH. The crown ethers selected were cryptand[2.2.1] (**9a**), 18-crown-6

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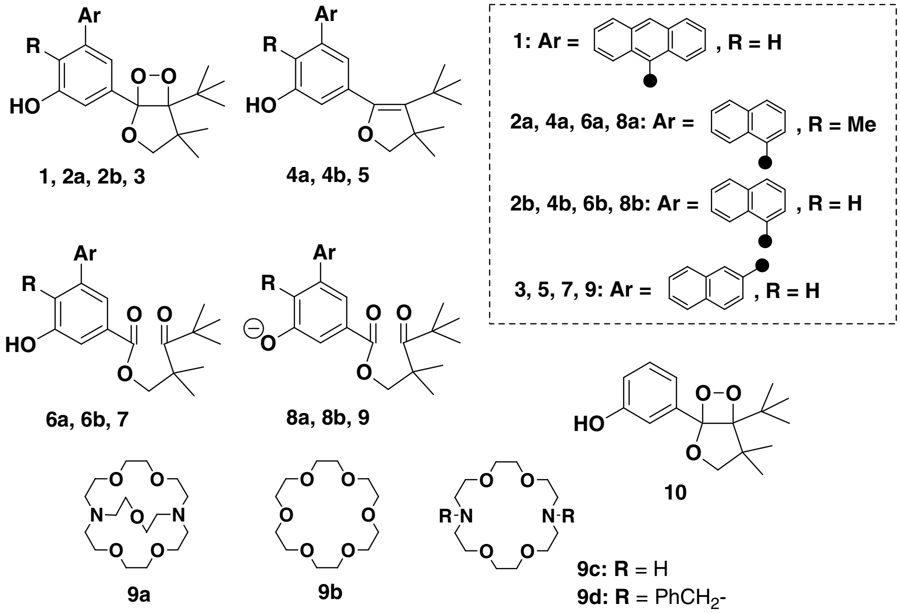

Figure 1.

Table 1. Color modulation for base-induced chemiluminescence of dioxetanes **2a**, **2b**, **3**, **10**, and **11**[a]

Dioxetane	Maximum wavelength λ_{max}^{CTICL}/ nm (Maximum wave number ν_{max}^{CTICL}/1000 cm^{-1})					
	TBAF	TBA^+B^{-b}	$[K \subset (\mathbf{9a})]^+B^-$	$[K \subset (\mathbf{9b})]^+B^-$	$[K \subset (\mathbf{9c})]^+B^-$	$[K \subset (\mathbf{9d})]^+B^-$
2a	582 (17.2)	615 (16.3)	599 (16.7)	551 (18.1)	477, 654 (21.0, 15.3)	530 (18.9)
2b	553 (18.1)	569 (17.6)	573 (17.5)	524, 585 (19.1, 17.1)	500, 622 (20.0, 16.1)	461 (21.7)
3	532 (18.8)	573 (17.5)	562 (17.8)	585 (17.1)	585 (17.1)	467, 569 (21.4–17.6)
10	467 (21.4)	478 (20.9)	472 (21.2)	486 (20.6)	472 (21.2)	470 (21.3)
11	580 (17.2)	618 (16.2)	619 (16.2)	565 (17.7)	560, 655 (17.9, 15.3)	464 (21.6)

[a] CTICL decomposition was carried out at 25 °C.
[b] B^- means t-BuO$^-$.

(**9b**), 4,13-diaza-18-crown-6 (**9c**), and *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 (**9d**). Complexation strengths of these crown ethers would be in the order of **9a** > **9b** > **9d** > **9c**, reflecting the reported[8–10] stability constants (*K*s). Therefore, the order of interaction between the naphthylphenoxide anion and central potassium ion may become inversely **9a** < **9b** < **9d** < **9c**. On the other hand, sizes of crown ethers **9a**–**9c** are apparently little different from each other, though **9d** having benzyl groups is far bulkier than the others.[11]

Chemiluminescent spectra for **2a** in $[K \subset (\text{crown ether})]^+t$-BuO$^-$/PhH systems are illustrated in Figure 2, and their λ_{max}^{CTICL}s and maximum wave numbers (ν_{max}^{CTICL}) are summarized in Table 1. These results show that λ_{max}^{CTICL}s for $[K \subset (\text{crown ether})]^+t$-BuO$^-$ shifted to blue from the case for TBA^+t-BuO$^-$, except for $[K \subset (\mathbf{9c})]^+t$-BuO$^-$. The magnitude of shift of λ_{max}^{CTICL} or ν_{max}^{CTICL} was in the order of $[K \subset (\mathbf{9a})]^+t$-BuO$^-$ < $[K \subset (\mathbf{9b})]^+t$-BuO$^-$ < $[K \subset (\mathbf{9d})]$ as illustrated in Figure 3. It should be noted that the maximum shift of ν_{max}^{CTICL} from that for TBA^+t-BuO$^-$ as a reference reached 2600 cm^{-1} (31 kJ mol^{-1}) (vide infra). The value was larger than the case of **1**, in which the maximum shift of ν_{max}^{CTICL} has been reported to be ca 2400 cm^{-1} (29 kJ mol^{-1}).[4] The case of $[K \subset (\mathbf{9c})]^+t$-BuO$^-$ displayed chemiluminescent spectrum with two peaks at 477 and 654 nm as shown in Table 1, Figures 2 and 3. The breadth of the split was surprisingly 5700 cm^{-1} (68 kJ mol^{-1}). Such phenomenon is presumably unprecedented for CTICL of dioxetanes.

The color modulation of CTICL from **1** and **2a** in the coordination sphere of crown ether should be attributed to the change of the dihedral angle of the arylphenol depending on repulsion of a wing of the anthracene or naphthalene ring with the face of the crown ether complex. Differently from the anthracen-9-yl ring, the naphthalen-1-yl ring is unsymmetrical around the bond joining to hydroxyphenyl in **2a**, and has a long wing and a short wing. The long wing would cause steric repulsion between the crown ether similar to the case of anthracene, whereas the short wing would not do so. Therefore, whether the naphthylphenol coordinates from the side of the long wing or from the side of the short wing should reflect directly on the conformation of the biaryl system. This is presumably the case of $[K \subset (\mathbf{9c})]^+t$-BuO$^-$. It should be pointed out here that chemiluminescent spectra were rather broader for $[K \subset (\mathbf{9a})]^+$ and $[K \subset (\mathbf{9d})]^+$ than for the TBA^+t-BuO$^-$

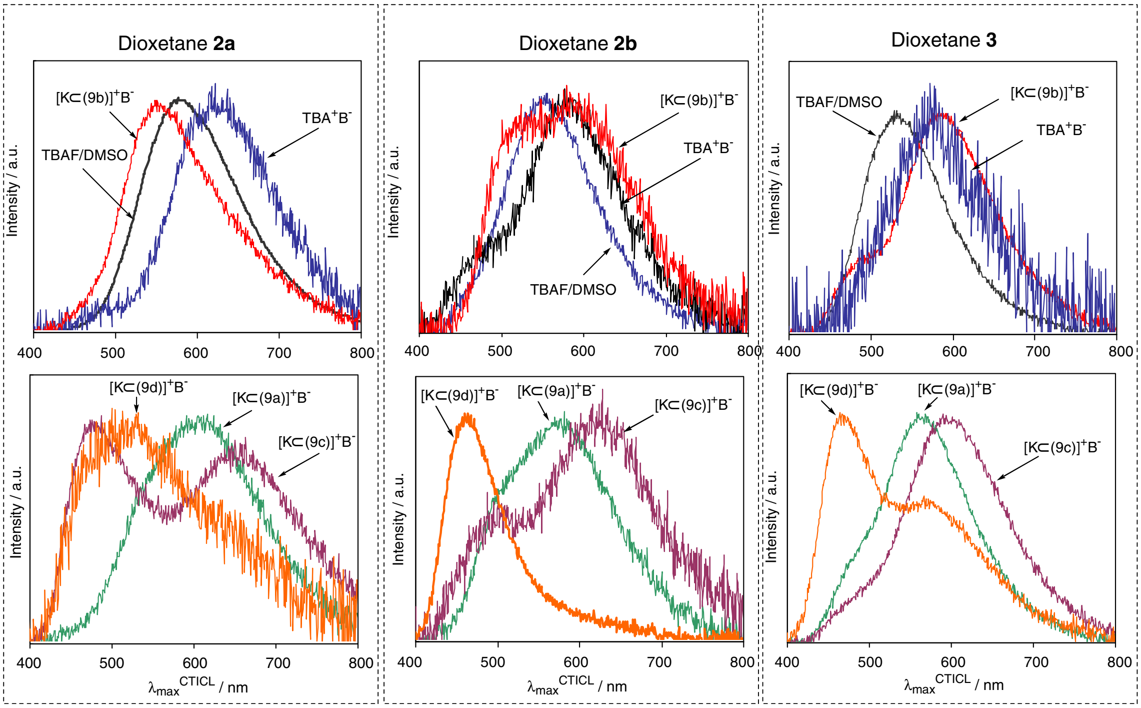

Figure 2. Chemiluminescent spectra of dioxetanes **2a**, **2b**, and **3** in various base systems.

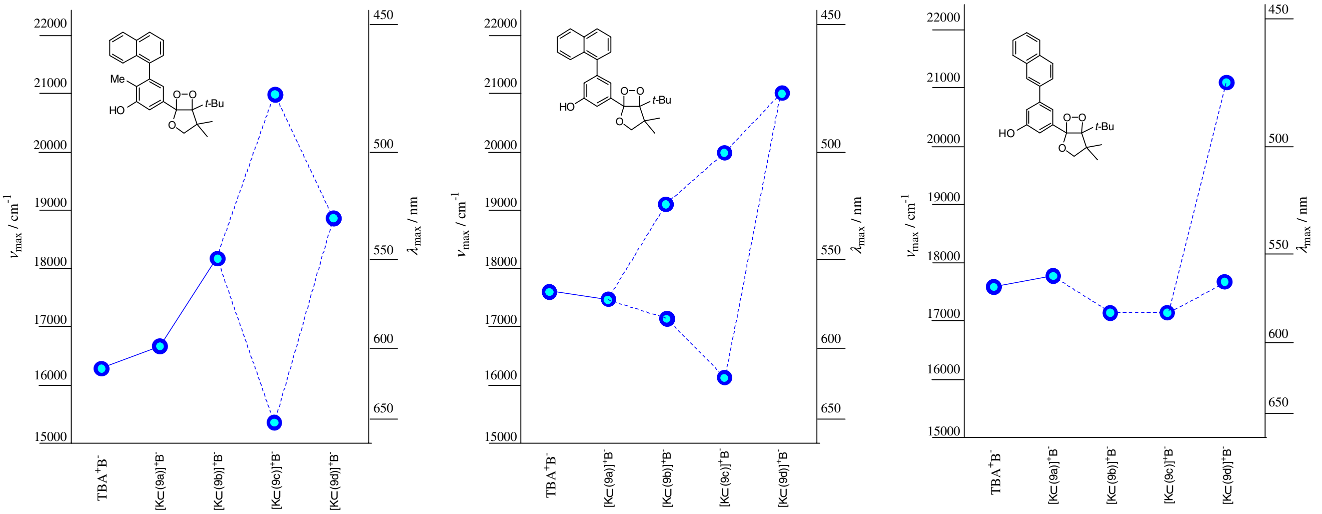

Figure 3. Relationship of $\lambda_{\max}^{\mathrm{CTICL}}$ and $\nu_{\max}^{\mathrm{CTICL}}$ with base-systems.

system. This means that the naphthyl of **2a** lies presumably in some conformations but not a specific one for these crown ether systems.

According to an AM1 MO calculation, dihedral angle θ of the naphthylphenol in a stable conformer for **2a** is estimated to be 74°, while it is 59° for **2b**. Therefore, steric interaction of the naphthalene ring with the crown ether should become smaller for **2b** than for **2a** on complexation. Furthermore, rotation of the naphthalene ring around the axis joining to the phenol should become easier for **2b**, for which 4-methyl is replaced by hydrogen in the 3-hydroxyphenyl group. When **2b** was treated in various base-systems, it decomposed to emit light, the spectra of which are illustrated in Figure 2. Their $\lambda_{\max}^{\mathrm{CTICL}}$s are also summarized in Table 1 and illustrated in Figure 3. Characteristic features of CTICL for **2b** are as follows. First, the breadth of color modulation was narrower for **2b** than for **2a**. Secondly, $[\mathrm{K} \subset (\mathbf{9d})]^+$ caused a large blue shift of the chemiluminescent spectrum of **2b** similar to the case of **2a**. Thirdly, a split into two peaks in the chemiluminescent spectrum was observed for $[\mathrm{K} \subset (\mathbf{9b})]^+$ in addition to for $[\mathrm{K} \subset (\mathbf{9c})]^+$, though the width of the split was narrower than in the case of **2a**.

The naphthalen-2-yl ring is also unsymmetrical, though the difference in bulk between the wings is quite small especially near the oxidophenyl anion center for **3**. In fact, it was suggested by AM1 MO calculation for **3** that the dihedral angle of the naphthylphenol was the smallest ($\theta = 38°$) in a stable conformation, and the naphthyl ring can rotate most easily among those for **2a**, **2b**, and **3**. Therefore, the steric interaction between naphthyl and crown ether would be the smallest among them under coordination with $[\mathrm{K} \subset (\mathbf{9})]^+$. Thus, CTICL decomposition of **3** was examined in $[\mathrm{K} \subset (\text{crown ether})]^+/\mathrm{PhH}$ systems as well as in the $\mathrm{TBA}^+t\text{-BuO}^-/\mathrm{PhH}$ system. The chemiluminescent spectra are shown in Figure 2, and $\lambda_{\max}^{\mathrm{CTICL}}$s are summarized in Table 1 and illustrated in Figure 3. These show that color modulation of chemiluminescence was not so much for $[\mathrm{K} \subset (\mathbf{9a})]^+$, $[\mathrm{K} \subset (\mathbf{9b})]^+$, and $[\mathrm{K} \subset (\mathbf{9c})]^+$, as expected, and only the most bulky $[\mathrm{K} \subset (\mathbf{9d})]^+$ caused a split of the peaks in the chemiluminescent spectrum.

It is believed that dioxetanes **2a, 2b**, and **3** produce the corresponding excited anionic keto esters **8a**, **8b**, and **9** even in the $[\mathrm{K} \subset (\text{crown ether})]^+t\text{-BuO}^-/\mathrm{PhH}$ system. However, the fluorescence spectra of **8a**, **8b**, and **9** generated from authentic emitters **6a**, **6b**, and **7** did not coincide with the respective chemiluminescent spectra of **2a, 2b**, and **3** in $[\mathrm{K} \subset (\text{crown ether})]^+t\text{-BuO}^-/\mathrm{PhH}$ system. For example, **8a** generated from **6a** displayed fluorescence spectra with a single peak (maximum wavelength, $\lambda_{\max}^{\mathrm{fl}}$) at 477–482 nm irrespective of $[\mathrm{K} \subset (\text{crown ether})]^+t\text{-BuO}^-$ in PhH, though chemiluminescence of **2a** was observed at $\lambda_{\max}^{\mathrm{CTICL}} = 477\text{–}654$ nm. These results suggest that the emitter produced by CTICL decomposition of dioxetane coordinated to $[\mathrm{K} \subset (\text{crown ether})]^+$ possesses presumably a transient structure, which retains the afterimage of conformation of the dioxetane ring to some extent.

According to this suggestion, the chemiluminescent spectrum should reflect both the structure of dioxetane and its conformation relative to the oxidophenyl ring coordinated to the central potassium ion. Thus, we synthesized, as a reference of **2a**, dioxetane **11**, which cleaves into two fragments, namely, benzoate **12** in an excited state and adamantanone, differently from **2a**. Dioxetane **11** decomposed to afford light with $\lambda_{\max}^{\mathrm{CTICL}} = 580$ nm in TBAF/DMSO, while it emitted light with $\lambda_{\max}^{\mathrm{CTICL}} = 618$ nm in $\mathrm{TBA}^+t\text{-BuO}^-/\mathrm{PhH}$ (Fig. 4). These $\lambda_{\max}^{\mathrm{CTICL}}$s coincided practically with those for **2a**. The tendency of color modulation and split of $\lambda_{\max}^{\mathrm{CTICL}}$ for CTICL of **11** was also similar to the case of **2a** in $[\mathrm{K} \subset (\mathbf{9a})]^+$, $[\mathrm{K} \subset (\mathbf{9b})]^+$, and $[\mathrm{K} \subset (\mathbf{9c})]^+$ systems, though $\lambda_{\max}^{\mathrm{CTICL}}$s were observed in a little longer wavelength region, as shown in Table 1. On the other hand, $[\mathrm{K} \subset (\mathbf{9d})]^+$ caused significant blue shift of chemiluminescence from **11**, that is, $\lambda_{\max}^{\mathrm{CTICL}} = 464$ nm for **11**, while $\lambda_{\max}^{\mathrm{CTICL}} = 530$ nm for **2a**. For these crown ether complex systems, significant discrepancy between chemiluminescent spectra and fluorescence spectra of authentic emitters was observed: authentic **12** generated from **13** displayed fluorescence spectra with $\lambda_{\max}^{\mathrm{fl}}$ at 479–485 nm, which did not coincide with the corresponding chemiluminescent spectra. These results support strongly the suggestion that chemiluminescence in the coordination sphere reflects the transient structure of dioxetane in CTICL decomposition (Fig. 5).

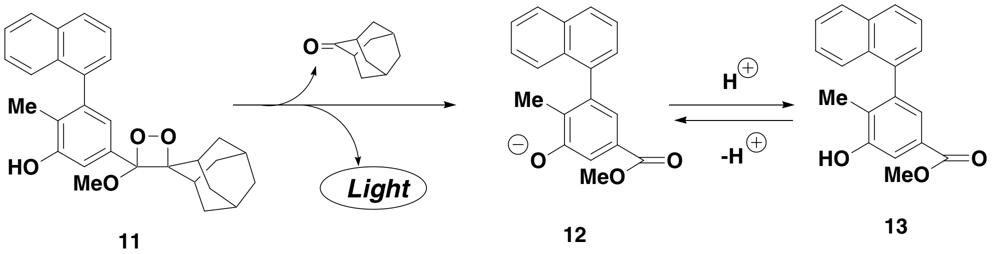

Figure 4.

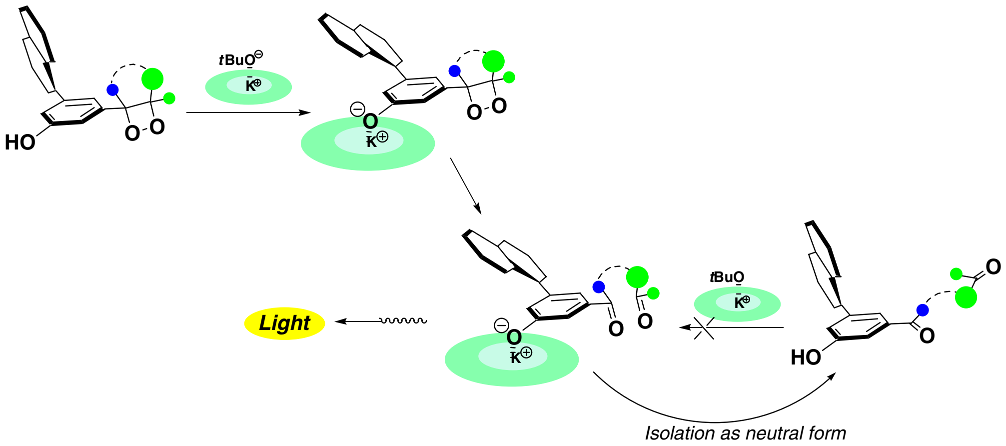

Figure 5.

In conclusion, dioxetanes bearing a 3-hydroxy-5-naphthyl moiety were found to undergo CTICL decomposition to emit light, $\lambda_{\max}^{\text{CTICL}}$ of which changed significantly depending on the base system used, and they exhibited chemiluminescence with split of $\lambda_{\max}^{\text{CTICL}}$ in some cases. The significant discrepancy between $\lambda_{\max}^{\text{CTICL}}$ and $\lambda_{\max}^{\text{fl}}$ of an authentic emitter was characteristic for CTICL of **2a**, **2b**, **3**, and **11** in the coordination sphere of the crown ether. The phenomenon indicates presumably that the structure of the emitter produced in CTICL retains afterimage of the structure of the dioxetane, which could be never reproduced from the authentic emitter.

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5. Selected data for **2a**: colorless granules, mp 146.5–147.5 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ_{H} 1.07 (s, 9H), 1.13 (s, 3H), 1.33 (s, 3H), 1.91 (s, 3H), 3.76 (d, $J = 8.2$ Hz, 1H), 4.56 (d, $J = 8.2$ Hz, 1H), 4.95 (s, 1H), 7.14 (s with fine coupling, 1H), 7.17 (s with fine coupling, 1H), 7.24–7.28 (m, 1H), 7.35–7.54 (m, 4H), 7.87 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ_{C} 12.9, 18.5, 25.0, 27.0, 36.8, 45.6, 80.1, 105.0, 114.1, 116.6, 123.1, 124.8, 125.3, 125.8, 126.1, 126.1, 126.6, 127.7, 128.2, 131.9, 133.4, 134.0, 139.0, 141.6, 153.5 ppm. Selected data for **2b**: colorless granules, mp 157.0–158.0 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ_{H} 1.09 (s, 9H), 1.15 (s, 3H), 1.34 (s, 3H), 3.80 (d, $J = 8.2$ Hz, 1H), 4.59 (d, $J = 8.2$ Hz, 1H), 5.05 (s, 1H), 6.98 (s with fine coupling, 1H), 7.21 (s with fine coupling, 1H), 7.32 (s, 1H), 7.36–7.53 (m, 4H), 7.83 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ_{C} 18.5, 25.1, 27.0, 36.9, 45.7, 80.2, 105.1, 114.4, 116.4, 118.1, 122.7, 125.2, 125.8, 125.8, 126.1, 126.8, 127.9, 128.2, 131.4, 133.6, 137.6, 139.2, 142.1, 154.9 ppm. Selected data for **3**: colorless granules, mp 147.0–147.5 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ_{H} 1.06 (s, 9H), 1.18 (s, 3H), 1.41 (s, 3H), 3.86 (d, $J = 8.2$ Hz, 1H), 4.62 (d, $J = 8.2$ Hz, 1H), 5.03 (s, 1H), 7.12 (s with fine coupling, 1H), 7.22 (s with fine coupling, 1H), 7.46–7.54 (m, 2H), 7.57 (br s, 1H), 7.70 (dd, $J = 8.5$ and 1.7 Hz, 1H), 7.83–7.93 (m, 3H), 8.01 (s with fine coupling, 1H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ_{C} 18.5, 25.1, 26.9, 36.8, 45.6, 80.3, 105.2, 114.4, 115.6, 116.6, 120.0, 125.3, 125.9, 126.1, 126.4, 127.6, 128.2, 128.5, 132.8, 133.5, 137.5, 138.0, 142.5, 155.7 ppm.
6. Chemiluminescent efficiencies were based on the value for 3-(3-*tert*-butyldimethylsiloxy)-3-methoxy-4-(2′-spiroadamantane)-1,2-dioxetane ($\Phi^{\text{CTICL}} = 0.29$).[7]
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