

Photosensitive luminol derivatives and measurement of ultraviolet ray power

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Abstract

We synthesized photosensitive luminol derivatives which had photoremovable protecting groups on the carbonyl oxygen of luminol to measure ultraviolet ray power. The photosensitive luminol derivatives released luminol by irradiation. The amount of released luminol increased with an increase in light power. Among the derivatives irradiated, photolysis of luminol-*O*-4'-methyl-7'-methoxycoumarin proceeded with a quantum yield of 0.035. The light power measurement with luminol-*O*-2-nitrobenzylate had a linear power range (0.8–6.5 J cm⁻²) and was applied to solar light power measurement.

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1. Introduction

Recently, various compounds which respond to light have been developed. Photosensitive compounds have been used for DNA synthesis and for investigating the roles of bioactive compounds in living cells. For example, Ohtsuka et al. reported the synthesis of 2'-*O*-(*o*-nitrobenzyl)uridine with deprotection of the *o*-nitrobenzyl group by photoirradiation [1]. Photosensitive esters of adenosine cyclic-3',5'-monophosphate (cAMP) were developed for investigating the biological response regulated by intracellular cAMP [2]. Nitrobenzyl, anthraquinone and coumarin moieties have been used as photoremovable protecting groups [2–4].

Chemiluminescent (CL) reagents have been used for highly sensitive methods not requiring a light source [5,6]. Especially, 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol) has a strong CL intensity in the presence of H₂O₂ and NaOH compared to that of other CL reagents. Luminol emits at approximately 420 nm, and the CL species is the 3-aminophthalate dianion [7,8]. The luminol derivative which has a methyl group on the carbonyl oxygen of luminol was nonchemiluminescent [9]. This means that the nonchemiluminescent and pho-

tosensitive luminol derivative, which releases luminol by irradiation, can be synthesized. More recently, we reported that luminol-*O*-2-nitrobenzylate (**1**) and luminol-*O*-4,5-dimethoxy-2-nitrobenzylate (**2**) could release luminol by irradiation [10,11].

The investigation of DNA and skin damage produced by the ultraviolet (UV) irradiation of sunlight has been the focus of DNA repair research. For example, UV light-induced DNA damage causes cell death, and UV-A light (320–400 nm) produces mutagenic oxidative DNA damage [12,13]. There have been no reagents that measured the UV power of sunlight. We assume that the development of a CL reagent which can measure UV light power simply and inexpensively is fascinating for the development of a novel functional CL molecule and can contribute to human health.

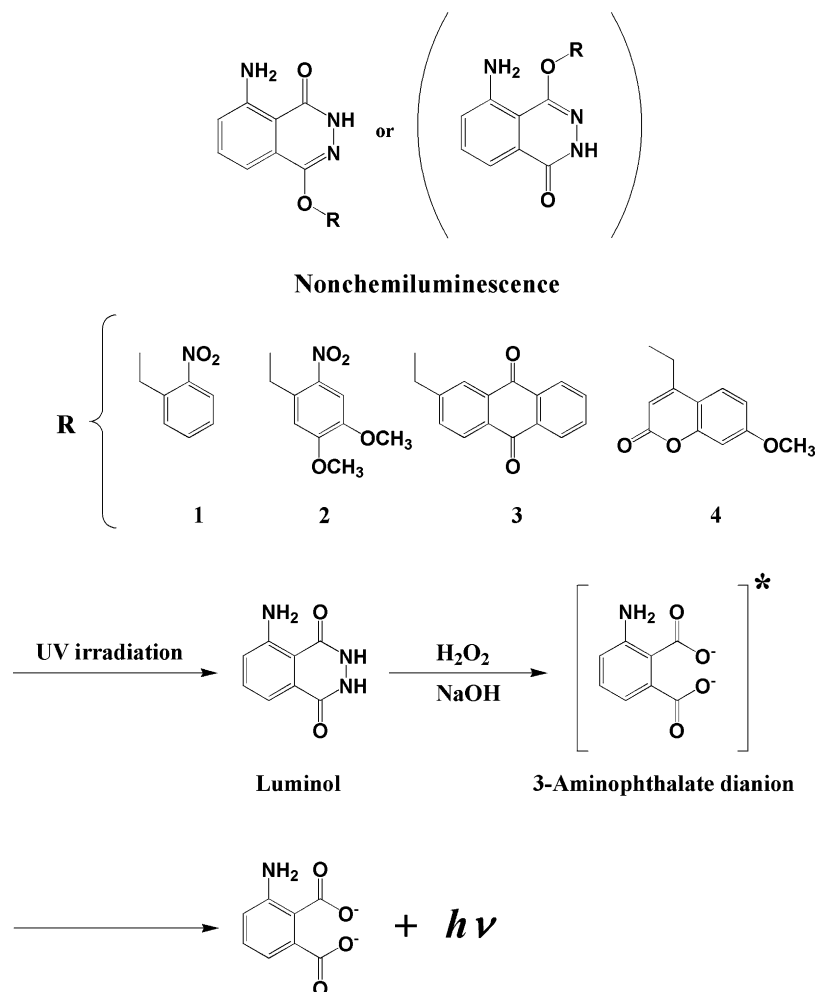
In this study, we newly synthesized photosensitive luminol derivatives which have one anthraquinone or coumarin moiety on the carbonyl oxygen of luminol and estimated the photosensitivities by irradiation (Scheme 1).

2. Experimental

2.1. Reagents

2-Nitrobenzyl chloride, sodium hydride (60% in oil) and dimethylformamide (DMF) were purchased from Wako Chemi-

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Scheme 1. Photolysis of luminol derivatives by UV irradiation and the CL mechanism of luminol.

cals (Osaka, Japan). 4,5-Dimethoxy-2-nitrobenzyl bromide and 2-(chloromethyl)anthraquinone were purchased from Aldrich (Milwaukee, USA). 4-Bromomethyl-7-methoxycoumarin and 2-(hydroxymethyl)anthraquinone were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). All other chemicals and solvents were of analytical reagent grade.

2.2. Apparatus

The ^1H NMR spectra were taken using a Varian UNITY plus (USA) spectrometer at 500 MHz. The FAB MS spectra of **1–4** were obtained using a JEOL JMS 600 (Tokyo, Japan). The photoirradiation system consisting of an Optical Module X (model SX-UI500 MQQ) and a power supply unit (model BA-H500) (360-nm cutoff and the distance between the collimator lens and the quartz cell was 40 cm) was obtained from USIO Electronics (Tokyo, Japan). The light power was changed by adjusting the lamp current or the distance between the collimator lens and the quartz cell. A cutoff filter of 360 nm was purchased from Stream (Saitama, Japan). A light power meter was purchased from Advantest (Tokyo, Japan). Reversed phase HPLC was conducted using a JASCO (Tokyo, Japan) PU-980 pump equipped with a Rheodyne 7725i syringe-loading sam-

ple injector valve (5-ml loop), a TSK-gel ODS-120T (25 mm i.d. \times 250 mm, Tosoh, Tokyo, Japan) column, and a JASCO CO-2065 Plus (operated at 60 °C) column oven, a UV-970 (operated at 280 nm) detector and a JASCO 807-IT integrator. A Hitachi F2000 (Tokyo, Japan) fluorometer was used for investigating the effect on the irradiation wavelength of **1–4** with a quartz cell (10 mm \times 10 mm \times 40 mm). Lumat LB 9501 (Berthold, Wildbad, Germany) was used to measure the CL with a round-bottom glass tube (75 mm \times 12 mm i.d.).

2.3. Synthesis

2.3.1. Luminol-*O*-2-nitrobenzylate (**1**) and luminol-*O*-4,5-dimethoxy-2-nitrobenzylate (**2**)

Luminol-*O*-2-nitrobenzylate (**1**) and luminol-*O*-4,5-dimethoxy-2-nitrobenzylate (**2**) were synthesized by the reported method [10,11].

2.3.2. Luminol-*O*-2'-methylantraquinone (**3**)

To stirred DMF (70 ml) were added luminol (0.44 g, 2.5 mmol) and sodium hydride (60% in oil, 0.2 g, 5 mmol), and the solution was then stirred at ambient temperature for 10 min. 2-(Chloromethyl)anthraquinone (0.77 g, 3 mmol) was added to

the solution, and the mixture was stirred at ambient temperature for 22 h. H₂O (250 ml) was added to the solution, and the organic layer was extracted with ethyl acetate (600 ml). To the organic layer was added CH₃OH (300 ml), the solution was dried over magnesium sulfate, and the filtrate was concentrated. The resulting precipitate was recrystallized from DMF–CH₃OH (1:4, v/v, 1800 ml) to give **3** as a yellow powder (0.05 g, 5.1% yield, mp > 300 °C). ¹H NMR ((CD₃)₂S=O): 5.52 (s, 2H, –OCH₂–Ph), 6.93 (d, 1H, *J* = 7.5 Hz, ArH), 7.03 (d, 1H, *J* = 7.5 Hz, ArH), 7.35 (brs, 2H, NH₂), 7.51 (t, 1H, *J* = 8 Hz, ArH), 7.93 (m, 2H, ArH), 8.00 (d, 1H, *J* = 7 Hz, ArH), 8.20 (m, 4H, ArH), 11.5 (s, 1H, –CO–NH–). FAB MS: 398.1 [*M* + H]⁺, anal. calcd. for C₂₃H₁₅O₄N₃·13/5 Na: C, 60.43; H, 3.31; N, 9.19. Found: C, 60.45; H, 3.31; N, 8.94.

2.3.3. Luminol-*O*-4'-methyl-7'-methoxycoumarin (**4**)

To stirred DMF (100 ml) were added luminol (0.12 g, 0.7 mmol) and sodium hydride (60% in oil, 0.028 g, 0.7 mmol), and the solution was then stirred at ambient temperature for 10 min. 4-Bromomethyl-7-methoxycoumarin (0.19 g, 0.7 mmol) was added to the solution. The mixture was stirred at ambient temperature for 22 h. H₂O (200 ml) was added to the solution, and the organic layer was extracted with ethyl acetate (400 ml). The organic layer was dried over magnesium sulfate, and the filtrate was concentrated. The resulting precipitate was recrystallized from CH₃OH–DMF (3:1, v/v, 800 ml) and purified by reversed phase HPLC (mobile phase, 60–77% CH₃CN gradient in H₂O, 80 min; flow rate, 3 ml/min; injection volume, 1 ml; retention time, 33.5 min) to give **4** as a yellow powder (0.01 g, 4% yield, mp > 300 °C). ¹H NMR ((CD₃)₂S=O): 3.86 (s, 3H, –OCH₃), 5.55 (s, 2H, –O–CH₂–), 6.35 (s, 1H, ArH), 6.93 (m, 3H, ArH), 7.35 (brs, 1H, ArH), 7.49 (t, 1H, *J* = 8.5 Hz, ArH), 7.70 (d, 1H, *J* = 8.5 Hz, ArH), 11.57 (s, 1H, –CO–NH–). FAB MS: 366.2 [*M* + H]⁺, anal. calcd. for C₁₉H₁₅O₅N₃·2Na: C, 55.48; H, 3.68; N, 10.22. Found: C, 55.18; H, 3.85; N, 9.60.

2.3.4. 4-Hydroxymethyl-7-methoxycoumarin (**5**) [14,15]

To stirred acetic anhydride (5 ml) were added 4-bromomethyl-7-methoxycoumarin (0.2 g, 0.74 mmol) and sodium acetate (0.7 g, 8.5 mmol), and the mixture was then refluxed for 5 h. After filtration and washing the residue with boiling acetic anhydride (4 ml), the resulting filtrate was poured onto ice (20 g) after being cooled. The solution was then stirred for 3 h. The solution was left at 4 °C overnight and filtered. The resulting precipitate was purified by column chromatography (silica gel, CHCl₃) to give 4-acetoxymethyl-7-methoxycoumarin as a colorless powder (0.07 g, 39% yield, mp 169 °C). To stirred EtOH–35% HCl (2/1, v/v, 15 ml) was added 4-acetoxymethyl-7-methoxycoumarin (0.07 g, 0.28 mmol), and the solution was refluxed for 2 h. H₂O (30 ml) was added to the solution, and the organic layer was extracted with ethyl acetate (120 ml). The organic layer was dried with magnesium sulfate, and the filtrate was concentrated. The resulting precipitate was purified by column chromatography (silica gel, CHCl₃–CH₃OH, 10/1, v/v) to give **5** as colorless needles (0.05 g, 86% yield, mp 188–189 °C). Anal. calcd. for C₁₁H₁₀O₄: C, 64.07; H, 4.89. Found: C, 63.78; H, 5.00.

2.4. The quantum yields of **1–4**

Three milliliters of the 0.1 mM **1–3** or 0.01 mM **4** in DMF was placed into a quartz cell. The solution was irradiated for 3–1200 s to a 360-nm cutoff using an ultrahigh pressure mercury lamp (450 mJ cm^{–2} s^{–1}). A 50 μl sample of the irradiated solution was subjected to HPLC with detection at 280 nm. The quantum yields ($\phi_{\text{app}\phi_{365}}$) for the appearance of luminol upon 365-nm irradiation of **1–4** in photolysis were calculated by the following equation; $\phi = 0.3 (I_0 \times \epsilon \times 10^3 \times t_{50\%})$; I_0 , the incident light intensity in millimoles of photons (s^{–1} cm^{–2}); ϵ , molar extinction coefficient (M^{–1} cm^{–1}); $t_{50\%}$, the half-time of photolysis (s). The quantum yields ($\phi_{\text{dis}\phi_{365}}$) for the disappearance of the starting materials upon 365-nm irradiation of **1–4** in photolysis were calculated by the following equation; $\phi = 1/(I_0 \times \epsilon \times 10^3 \times t_{90\%})$; I_0 , the incident light intensity in millimoles of photons (s^{–1} cm^{–2}); ϵ , molar extinction coefficient (M^{–1} cm^{–1}); $t_{90\%}$, irradiation time for 90% conversion to the product (s). The yields of photolytic consumption of **1–4** and luminol release were calculated by the peak area in the HPLC chromatogram [16,17].

2.5. Photoirradiation of **1–4**

Three ml of the 1 μM **1**, **2** or **4** (10 μM **3**) in DMF was placed into a quartz cell. The solution was irradiated for 1–600 s with a 360-nm cutoff filter using an ultrahigh pressure mercury lamp (0.18–81 J cm^{–2}). To 200 μl of the irradiated solution was added 100 μl of 10 mM NaOH. After allowing the solution to stand for 25 s, 100 μl of 500 mM H₂O₂ was added to the mixture using the automatic injection system in the luminometer. The CL emission was measured for 5 min, and the integral photon counts were used for estimating the CL intensities. In this CL batch method, we should obtain the amount of luminol released by the irradiation of **1–4**. Upon the irradiation of **1–4**, 2-nitrosobenzaldehyde, 4,5-dimethoxy-2-nitrosobenzaldehyde, 2-(hydroxymethyl)anthraquinone or 4-hydroxymethyl-7-methoxycoumarin (**5**) may be possible photolysis byproducts, respectively. We could not synthesize 2-nitrosobenzaldehyde and 4,5-dimethoxy-2-nitrosobenzaldehyde. We found that the CL intensity of luminol in the presence of 2-(hydroxymethyl)anthraquinone or **5** was 80 or 20% compared to that in the absence of 2-(hydroxymethyl)anthraquinone or **5**. Thus, the amount of luminol released by irradiation of **1** and **2** was obtained from the calibration curve of luminol. The amount of luminol released by irradiation of **3** and **4** was obtained from the calibration curve of luminol in the presence of 2-(hydroxymethyl)anthraquinone and **5**. When all of the luminol amount was released by irradiation, the CL intensity of 200 pmol luminol was obtained during the CL measurement of the reaction solution after irradiation.

2.6. Effect of photoirradiation wavelength of **1–4**

Two milliliters of the 1 μM **1–4** in DMF was placed into a quartz cell. The solution was irradiated for 300 s in the range

of 260–420 nm using a Hitachi F2000 fluorometer. To 200 μl of the irradiated solution was added 100 μl of 10 mM NaOH. After allowing the solution to stand for 25 s, 100 μl of 500 mM H_2O_2 was added to the mixture using the automatic injection system in the luminometer. The CL emission was measured for 5 min, and the integral photon counts were used for estimating the CL intensities.

2.7. Solar irradiation of 1

Three ml of the 1 μM **1** in DMF was placed into a quartz cell. The solution was exposed to sunlight and irradiated on the ground (2.4 m above sea level) for 60 s. To 200 μl of the irradiated solution was added 100 μl of 10 mM NaOH. After allowing the solution to stand for 25 s, 100 μl of 500 mM H_2O_2 was added to the mixture using the automatic injection system in the luminometer. The CL emission was measured for 5 min, and the integral photon counts were used for estimating the CL intensities.

3. Results and discussion

3.1. Synthesis and structure of 1–4

Photosensitive luminol derivatives (**1–4**) were synthesized in one step. We could not obtain the **1–4** crystals usable for X-ray crystallography to determine the binding site of the photoremovable protecting groups of **1–4** on the two carbonyl groups of luminol. Thus, we could not determine the exact structures of **1–4**.

3.2. Photochemical characteristics of 1–4

The time course of the photolytic consumption and luminol release by the irradiation of **1–4** using an ultrahigh pressure mercury lamp is shown in Fig. 1. In the photolysis of **1–4**, **1–4** were not converted to luminol in a yield of 100%. The photochemical characteristics of **1–4** are shown in Table 1. In the spectroscopic measurements of **1–4**, the absorption of **1–4** was obtained from 260 to 400 nm. Among **1–4**, **3** had the highest molar extinction coefficient at 365 nm. The quantum yields ($\text{app}\phi_{365}$ and $\text{dis}\phi_{365}$) of **1–4** for the appearance of luminol and the disappearance of the starting materials were determined. The values of $\text{app}\phi_{365}$ and $\text{dis}\phi_{365}$ were not the same. This indi-

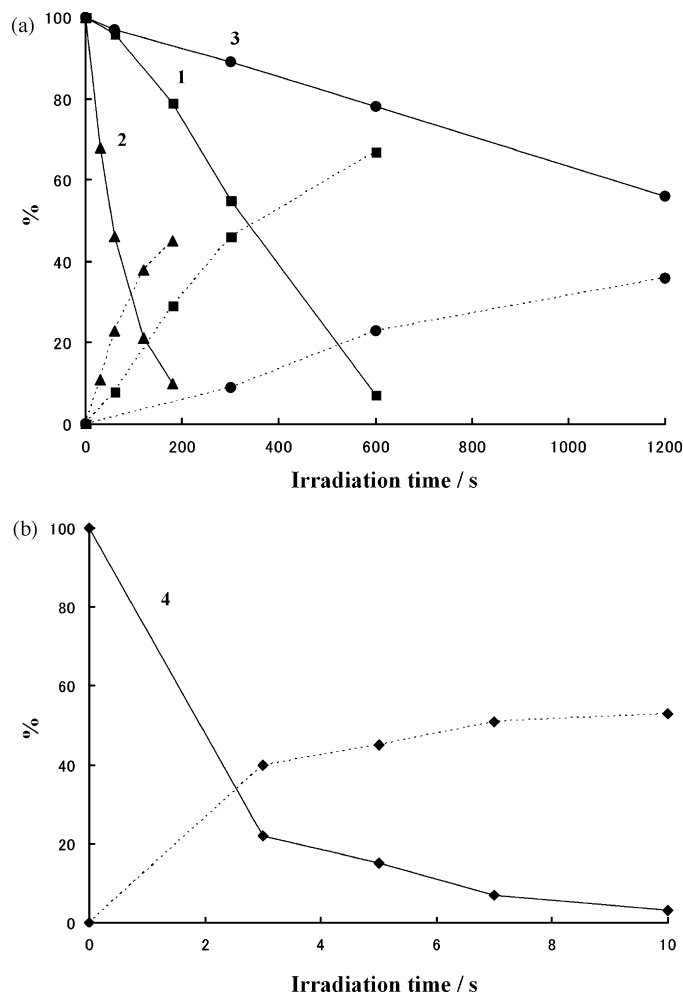


Fig. 1. Time course of the photolytic consumption and luminol release by the irradiation of **1–4** using an ultrahigh pressure mercury lamp. The solid line and dotted line represent the photolytic consumption and luminol release by the irradiation of **1–4**, respectively. The concentration of **1**, **2** or **3** in DMF was 0.1 mM. The concentration of **4** in DMF was 0.01 mM. **1** (■); **2** (▲); **3** (●); **4** (◆).

cated that the photolysis of **1–4** did not proceed perfectly. The quantum yields of **1** and **2** were low compared with that of photosensitive compounds which have a nitrobenzyl group as a photoremovable protecting group [18,19]. The quantum yield ($\text{dis}\phi_{365}$) of **4** was 0.035 and was the highest value among **1–4**. The $\epsilon_{365} \times \text{dis}\phi_{365}$ value, which indicates the efficiency of pho-

Table 1
Photochemical characteristics of **1–4**

	$\lambda_{\text{max}}^{\text{a}}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)	ϵ_{365} ($\text{M}^{-1} \text{cm}^{-1}$)	$\text{app}\phi_{365}^{\text{b}}$	$\text{dis}\phi_{365}^{\text{c}}$	$\epsilon_{365} \times \text{dis}\phi_{365}^{\text{d}}$
1	285 (2320)	1440	3.5×10^{-4}	9×10^{-4}	1.3
2	353 (2580)	2380	4.6×10^{-4}	1.7×10^{-3}	4
3	297 (9300)	6530	1.9×10^{-5}	2.4×10^{-5}	0.16
4	313 (10180)	3400	0.009	0.035	119

^a Absorption spectra were taken in 0.1 mM **1–4** in DMF.

^b Quantum yields for the appearance of luminol upon 365-nm irradiation.

^c Quantum yields for the disappearance of the starting materials upon 365-nm irradiation.

^d The value, which is a product of the quantum yield for the disappearance of the starting materials and the molar extinction coefficient, is an indication of the efficiency of the photolysis.

tolysis, was 119 and was much greater than that of **1–3** (Table 1). In contrast, the quantum yield ($\text{dis}\phi_{365}$) and $\varepsilon_{365} \times \text{dis}\phi_{365}$ of **3** were 2.4×10^{-5} and 0.16, respectively. These values were apparently low compared with that of photosensitive compounds which have an anthraquinone group as the photoremovable protecting group [2,20]. These results showed that the coumarin moiety is a photosensitive one which can efficiently release luminol. **1** and **2** may release luminol *via* the cyclic intermediates, i.e., the isoxazol-1-ol derivatives [21]. **4** may release luminol *via* the carbocation of 4-methyl-7-methoxycoumarin [22]. Thus, the differences in the photoremovable mechanism upon the photoirradiation of **1–4** should have a significant effect on the release of luminol. The photosensitive characteristics of various coumarin compounds have been studied. Especially, the 4-methyl-7-methoxycoumarin compounds showed a highly photocleavage characteristics in polar solvents such as CH_3OH and CH_3CN [14,22]. The reason that the photolysis efficiency of the anthraquinone group was apparently inferior to that of other photoremovable protecting groups we tested was unclear. The time course of the luminol release by the irradiation of **1–4** using an ultrahigh pressure mercury lamp is shown in Fig. 2. Upon the irradiation of **1–4** in $1 \mu\text{M}$, the luminol released was not detected with the HPLC-UV method. Therefore, we inves-

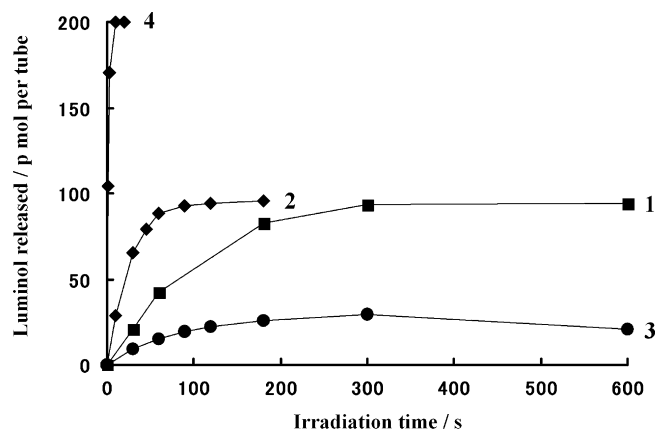


Fig. 2. Time course of the luminol release by the irradiation of **1–4** using an ultrahigh pressure mercury lamp. The concentration of **1**, **2** or **4** in DMF was $1 \mu\text{M}$. The concentration of **3** in DMF was $10 \mu\text{M}$. The concentrations of NaOH and H_2O_2 were respectively 10 mM and 500 mM under each CL reaction condition.

tigated the luminol release by a CL batch method which can detect luminol with higher sensitivity compared with the HPLC-UV method. **1**, **2** and **3** released almost the maximum amount of luminol with a light power of $450 \text{ mJ cm}^{-2} \text{ s}^{-1}$ and an irradi-

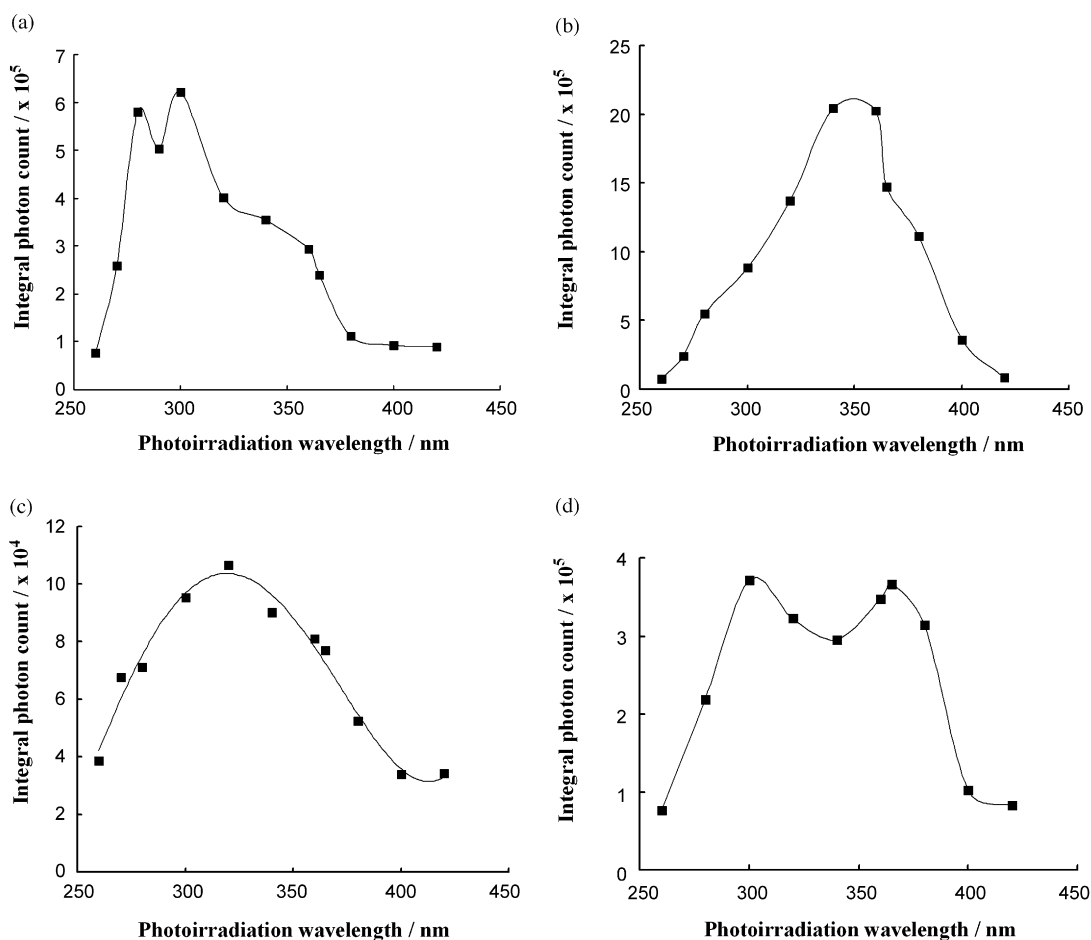


Fig. 3. Effect of photoirradiation wavelength of **1–4** using the fluorometer: (a) **1**; (b) **2**; (c) **3**; (d) **4**. The concentration of **1–4** in DMF was $1 \mu\text{M}$. The irradiation time of **1–4** was 300 s. The concentrations of NaOH and H_2O_2 were respectively 10 mM and 500 mM under each CL reaction condition. The light power of the Hitachi F2000 fluorometer was approximately 1 mW cm^{-2} .

ation time of 300, 180 and 300 s, respectively. At the specified time, the released amount of luminol from **1**, **2** and **3** reached 50, 50 or 1.5%, respectively. **3** required the longest irradiation time to release the luminol and released the least amount of luminol by irradiation. In contrast, **4** released almost all the luminol within the irradiation time of 10 s. The luminol release characteristics of **1–4** were almost similar in concentrations of 0.1 mM and 1 μ M.

3.3. Effect of photoirradiation wavelength of **1–4**

The effect of the photoirradiation wavelength of **1–4** is shown in Fig. 3. The CL intensities by irradiation at 260 and 420 nm were the same as those of **1–4** without irradiation. Thus, **1–4** released luminol by irradiation in the range of 270–400 nm.

3.4. Light power measurement with **1–4**

The light power measurement with **1–4** is shown in Fig. 4. The CL intensities by irradiation of **1–4** increased with an increase in light power. The calibration curve for released luminol by the irradiation of **3** was linear ($n=3$) and needed the highest light power among **1–4**. The calibration curve for released luminol by the irradiation of **2** was linear ($n=3$), and the linear range was not wider than that of **1** ($n=3$). The calibration curve for released luminol by the irradiation of **4** was not linear.

3.5. Solar light power measurement and change in solar light power within 1 day with **1**

The UV rays below 290 nm are absorbed by the ozone layer in the earth's atmosphere; therefore, UV rays at 290–400 nm do reach the earth's surface. From the measurement of the light power (0.18–81 J cm^{-2}) and irradiation wavelength (270–400 nm), which release luminol, **1** had a wide linear range (0.8–6.5 J cm^{-2}) in the light power measurement and was optimum for solar irradiation. We observed that **1** released luminol by solar irradiation. Solar light power measurement with **1** is shown in Fig. 5. The CL intensities by solar irradiation of **1** linearly increased with an increase in solar power. The calibration curve for solar light power with **1** was linear in the range of 2–60 J cm^{-2} ($n=3$). The release of luminol by the solar irradiation of **1** within 1 day is shown in Fig. 6. A solar irradiation time of 60 s was used, and the released amount of luminol reached a maximum at 11:00. The change in the UV power almost matched that of Fukuoka (Japan) which the Japan Metrological Agency reported on the same day. Similar results between the luminol released and the UV index at 12:00 and 13:00 were not obtained. The sunlight power measurement by our method at 12:00 and 13:00 was affected by clouds (Fig. 6). **1** released 2 pmol of luminol after a solar irradiation time of 60 s at 11:00. This indicated that **1** received a light power of 10 J cm^{-2} from the sun for 60 s at 11:00.

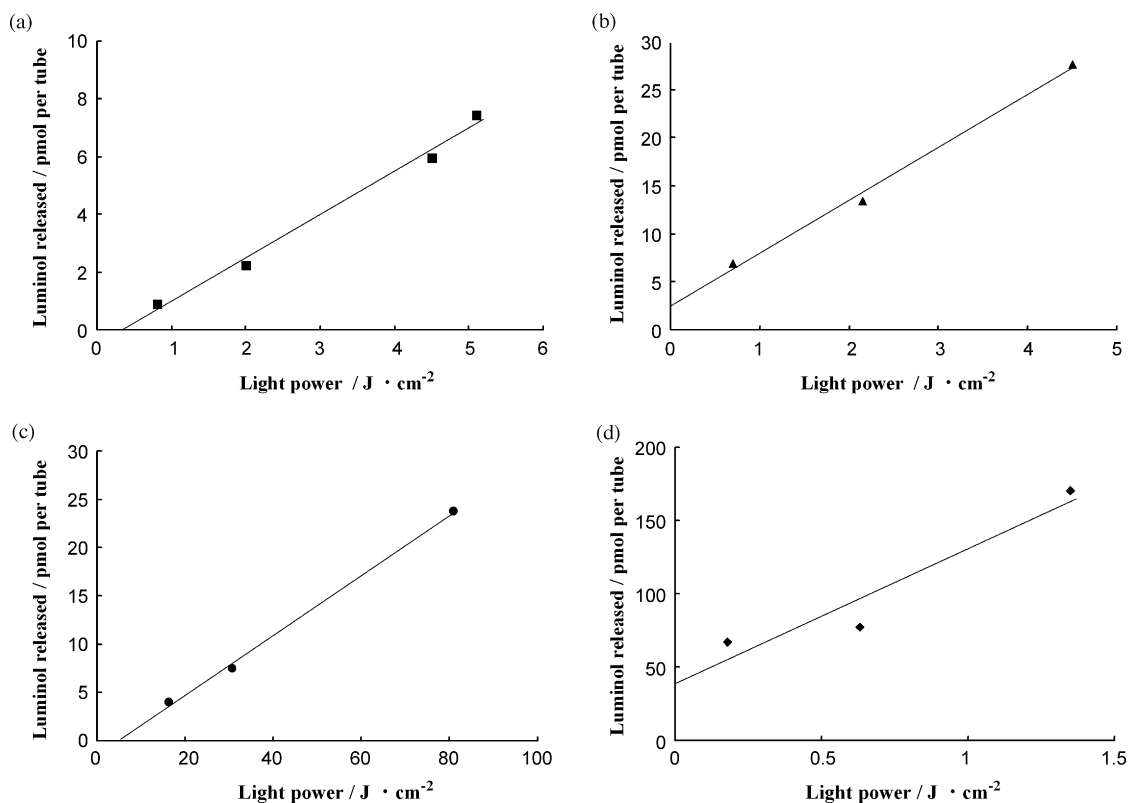


Fig. 4. Light power measurement with **1–4** using an ultrahigh pressure mercury lamp: (a) **1**; (b) **2**; (c) **3**; (d) **4**. The concentration of **1**, **2** or **4** in DMF was 1 μ M. The concentration of **3** in DMF was 10 μ M. The irradiation time of **1**, **2**, **3** or **4** was 10 s, 10 s, 180 s or 3 s. The concentrations of NaOH and H_2O_2 were respectively 10 mM and 500 mM under each CL reaction condition.

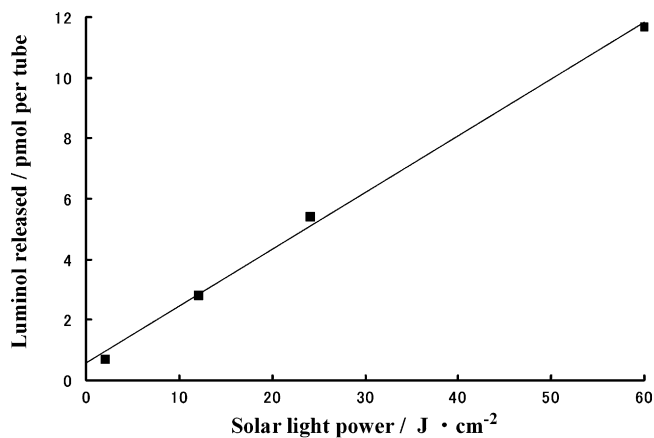


Fig. 5. Solar light power measurement with **1**. The irradiation time was 10 s, 60 s, 120 s or 300 s. The concentration of **1** in DMF was 1 μ M. The solar light power was 200 mW cm⁻² at 364 nm using a light power meter. The concentrations of NaOH and H₂O₂ were respectively 10 mM and 500 mM under each CL reaction condition.

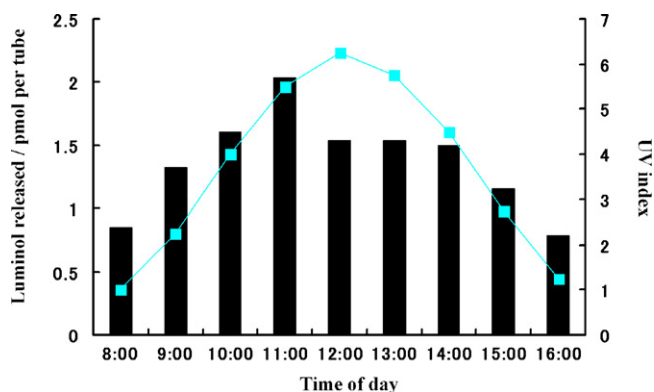


Fig. 6. Release of luminol by solar irradiation of **1** within 1 day. Black column and blue line represent the released amount of luminol and the UV index, respectively. The irradiation time was 60 s. The concentration of **1** in DMF was 1 μ M. The concentrations of NaOH and H₂O₂ were respectively 10 mM and 500 mM under each CL reaction condition. The UV index of Fukuoka in Japan was reported by the Japan Meteorological Agency in 26 September 2005.

4. Conclusions

We synthesized photosensitive luminol derivatives, examined their photochemical characteristics and evaluated their photosensitivities. We found that **1**, **2** or **3** could be used to measure

UV light power. Further investigations should be needed for the development of photosensitive luminol derivatives which have a wide linear UV range such as **1** and which efficiently release luminol such as **4** for measuring the UV power of sunlight. This study developed a novel CL method with luminol.

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