HETEROCYCLES, Vol. 104, No. 9, 2022, pp. 1614 - 1623. © 2022 The Japan Institute of Heterocyclic Chemistry
Received, 25th June, 2022, Accepted, 13th July, 2022, Published online, 15th July, 2022
DOI: 10.3987/COM-22-14703

SYNTHESIS OF 2,3-ANTHRACENEDICARBOXYLIC-ACID-DERIVED FLUOROPHORE AND CHEMILUMINOPHORE INCORPORATING DIPICOLYLAMINOMETHYL RECEPTORS, AND THEIR LUMINESCENCE RESPONSES TO METAL IONS†

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Abstract – 2,3-Anthracenedicarboxylic-acid-derived carboximide **1** and cyclic-hydrazide **2**, incorporating dipicolylaminomethyl receptors, have been respectively prepared as novel fluorescence and chemiluminescence probes for metal cations. Carboximide **1** was essentially non-fluorescent in acetonitrile whereas it produced intense fluorescence (λ_{FL}^{max} 470 nm) upon addition of Zn^{2+} (off–on response). Cyclic-hydrazide **2** gave off blue chemiluminescence emission (λ_{CL}^{max} 465 nm) after addition of alkaline H_2O_2 and iodide ion in dimethyl sulfoxide. Addition of metal cations, e.g. Zn^{2+}, into the chemiluminescence system resulted in significant quenching of the chemiluminescence (on–off response). Therefore, the effects of the metal cation on the chemiluminescence behavior of cyclic-hydrazide **2** showed clear contrast to those on the fluorescence behavior of carboximide **1**.

INTRODUCTION

Numbers of colorimetric and fluorometric probes for metal cations have been constructed because of their significance in analytical tools, bioprobes, sensors, and molecular logic circuits, etc.[1–9] Conventionally, guest-specific host functionalities have been combined with a signal-transduction moiety, such as chromophores and luminophores, to show responses to the guests. One of the most important strategies for the construction of luminescent probes is to utilize switching by photoinduced electron transfer (PET).[4,9] The pioneering system was reported by de Silva, for which an azacrown host functionality was bound to anthracene fluorophore through a methylene spacer [Chart 1, compound (i)].[10]

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† This paper is dedicated to Professor Dr. Waldemar Adam on the occasion of his 85th birthday.

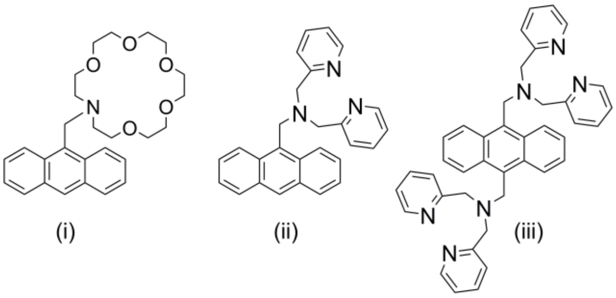


Chart 1. Examples of conventional anthracene-based fluorescent PET probes

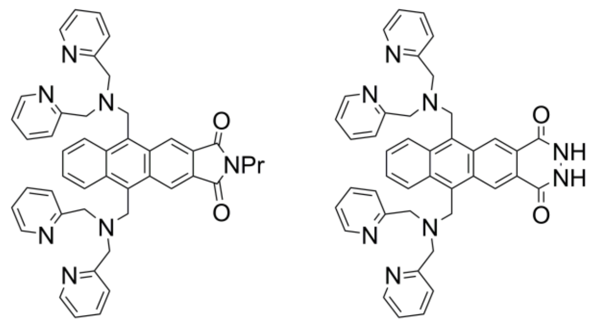
The azacrown moiety serves as an electron donor that quenches fluorescent state of anthracene resulting in weak or no fluorescence. Upon binding the donor with a specific metal cation, the PET quenching is inhibited resulting in intense fluorescence. According to the concept, dipicolyaminomethyl donor unit has been widely utilized to modify luminescent properties of PET probes, namely for transition metal cations [Chart 1, compounds (ii) and (iii)].[11,12]

Chemiluminescent dyes (chemiluminophores) are expected to be alternative signaling components for constructing luminescent probes. However, much less effort has been addressed to prepare chemiluminescent sensors which have a host functionality to respond to a specific guest. A few chemiluminophores incorporating crown ether moieties have been reported whose chemiluminescence feature were modified by alkali metal cations.[13–17]

Motoyoshiya et al. have investigated effects of host molecules, which possess dipicolylaminomethyl functionality as the electron donor, on a peroxalate chemiluminescence system.[18] They revealed that the host molecule effectively quenched the chemiluminescence, whereas addition of transition metal cations such as Zn^{2+} and Cu^{2+} to the chemiluminescence system recovered the chemiluminescence emission. These results suggest that chemiluminescence nature can also be controlled by PET switching and an appropriately modified chemiluminophore would serve as a novel sensing probe.

It would, thus, be of interest to construct a chemiluminophore incorporating dipicolylaminomethyl host moiety and to reveal whether natures of the chemically generated luminescent state can be manipulated by PET switching. Since anthracene-2,3-dicarbohydrazide has been known to be chemiluminenscent,[19,20] we attempted to modify the chemiluminophore with dipicolylaminomethyl host functionality to construct a novel luminescent probe.

In the present study, we modified anthracene-2,3-carboximide fluorophore and anthracene-2,3-carbohydrazide chemiluminophore with dipicolylaminomethyl (DPAM) functionality, compounds **1** and **2**, respectively, as shown in Chart 2 and investigated their luminescent behavior in the presence of metal cations.



1
(FL probe)

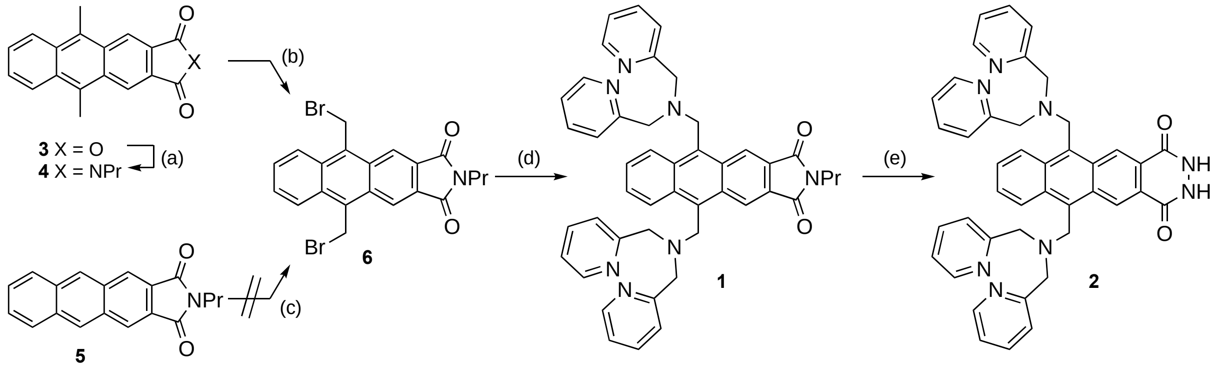
2
(CL probe)

Chart 2. Structures of carboximide **1** and cyclic-hydrazide **2**

RESULTS AND DISCUSSION

Preparations of DPAM-incorporating carboximide 1 and cyclic-hydrazide 2

The synthetic routes to compounds **1** and **2** are shown in Scheme 1. 9,10-Dimethyl-2,3-anthracenedicarboxylic anhydride **3** was prepared according to the reported procedure.[21] The anhydride **3** was treated with propylamine to afford compound **4** whose methyl groups were then brominated with *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide (BPO) to afford dibromide **6** (60% from **3**). Although direct bromomethylation of anthracenecarboxyimide **5** appeared to be more convenient to obtain dibromide **6**, a reaction of anthracenecarboximide **5** with paraformaldehyde and HBr in AcOH resulted in recovery of unreacted imide **5** instead of formation of desired dibromide **6**. This was presumably because that the electrophilic bromomethylation was prevented by the strongly electron-withdrawing imide functionality in the substrate **5**. The bromomethyl substituents in compound **6** were converted to DPAM functionality through a reaction with dipicolylamine affording the desired carboximide **1** in 36% yield. Subsequently, carboximide **1** was reacted with hydrazine to form cyclic-hydrazide **2** in 44% yield. The structures of carboximide **1** and cyclic-hydrazide **2** were confirmed by NMR and IR spectra as well as HRMS data.



Scheme 1. Synthetic routes to DPAM-modified carboximide **1** and cyclic-hydrazide **2**. Reagents and conditions: (a) PrNH$_2$, toluene, reflux, 15 h, then Ac$_2$O, heat, 62%; (b) NBS, BPO, CCl$_4$, reflux, 16 h, 96%; (c) (CH$_2$O)$_n$, HBr, AcOH, reflux; (d) dipicolylamine, KI, DMF, rt, 1 h, 36%; (e) hydrazine hydrate, EtOH, reflux, 21 h, 44%.

FLUORESCENCE BEHAVIOR OF CARBOXIMIDE 1

To elucidate responses of carboximide **1** to metal cations, its fluorescence (FL) spectra were measured in the presence of various metal cations (10 equiv.) in MeCN, and the results are shown in Figure 1. In the absence of an additive, carboximide **1** was essentially non fluorescent. Addition of Co^{2+}, Ni^{2+}, or Cu^{2+} displayed minimal effect to modify the FL spectra, thus these cations did not affect the FL properties of carboximide **1**. In contrast, addition of Mg^{2+} or Zn^{2+} resulted in appreciable enhancement of the FL intensity of carboximide **1**.

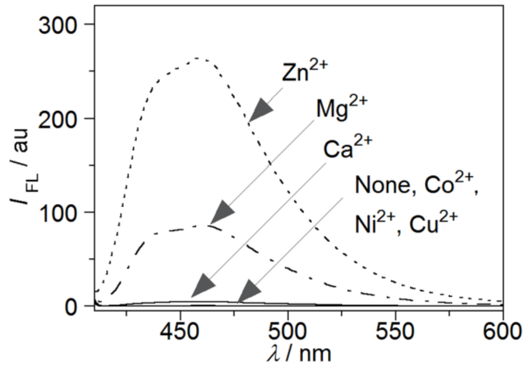


Figure 1. Effects of metal cations (10 equiv.) on the FL spectra (λ_{ex} 403 nm) of carboximide **1** (1.0×10^{-5} M) in MeCN

In order to understand detailed effects of Mg^{2+} and Zn^{2+} on the FL spectra of carboximide **1**, FL titration experiments with Mg^{2+} and Zn^{2+} were conducted at the concentration of [**1**] = 1.0×10^{-5} M (Figures 2a,b). The FL intensity of carboximide **1** increased by the addition of the metal cations; the spectral intensity enhanced upon the titration and saturated in the concentration region of $[Mg^{2+}] > 5.0 \times 10^{-4}$ M (> 50 equiv.) and $[Zn^{2+}] > 4.0 \times 10^{-5}$ M (> 4 equiv.) (Figure 2c). The stoichiometry of **1**-Zn^{2+} complexation was estimated to be 1 : 2 by continuous variation method (Figure S1). Fluorescence quantum yield Φ_F of carboximide **1** reached as high as 0.27 at $[Mg^{2+}] = 5.0 \times 10^{-4}$ M (50 equiv.) and 0.30 at $[Zn^{2+}] = 1.0 \times 10^{-4}$ M (10 equiv.). Thus, carboximide **1** serves as a fluorescence off-on probe for Zn^{2+} and Mg^{2+} as in the case of related DPAM-substituted antharacenes.[11,12] The FL enhancement by the metal cations can be well understood by inhibition of PET quenching with the DPAM functionality. From the fluorescence titration curves shown in Figure 2c, it is obvious that carboximide **1** displayed higher sensitivity toward Zn^{2+} than Mg^{2+}. The FL intensity of carboximide **1** was enhanced by 160-fold and 240-fold by addition of Mg^{2+} and Zn^{2+}, respectively.

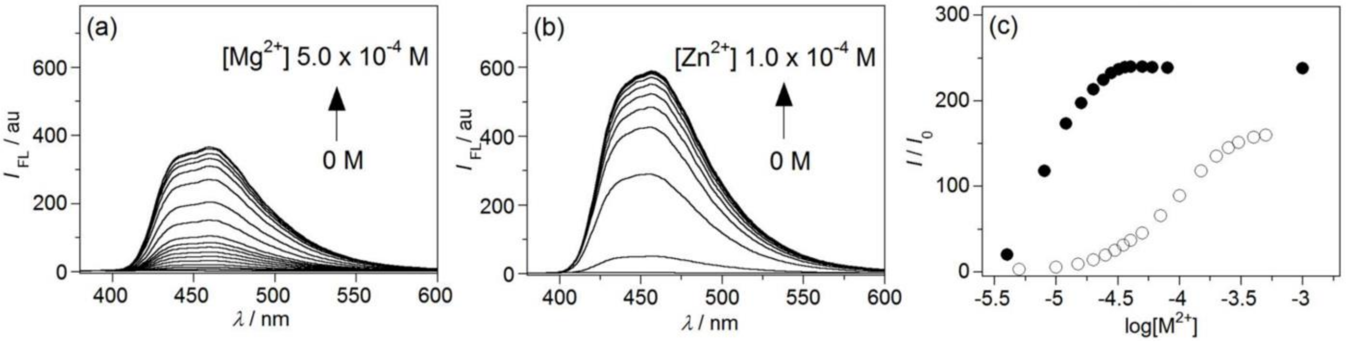


Figure 2. Effects of Mg^{2+} and Zn^{2+} on the FL spectra of carboximide **1** (1.0×10^{-5} M) in MeCN. (a) Mg^{2+} (0–5.0×10^{-4} M, λ_{ex} 350 nm), (b) Zn^{2+} (0–1.0×10^{-4} M, λ_{ex} 363 nm). (c) FL titration results for Mg^{2+} at λ_{FL} 456 nm (○) and Zn^{2+} at λ_{FL} 445 nm (●).

CHEMILUMINESCENCE BEHAVIOR OF CYCLIC-HYDRAZIDE 2

In order to reveal whether metal cations modify CL spectral behavior of cyclic-hydrazide **2**, its CL spectra were observed in the presence of metal cations. Figure 3 shows the CL spectra of cyclic-hydrazide **2** in DMSO observed upon oxidation with H_2O_2 under alkaline conditions in the presence of iodide ions. Cyclic-hydrazide **2** gave off naked-eye detectable, blue CL emission with a maximum wavelength at λ^{CL}_{max} 441 nm. In the presence of metal cations (200 equiv.), the CL emission was effectively quenched (on–off response). Even Mg^{2+} and Zn^{2+}, which effectively enhanced the FL intensity of carboximide **1**, quenched the CL emission. Therefore, the effects these cations on the CL of cyclic-hydrazide **2** are different than those on the FL of carboximide **1**. Among the metal cations investigated, addition of Mg^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} completely quenched the CL emission, whereas, that of Zn^{2+} retained a week CL emission band (Figure 3a). The time profile of the CL reaction was observed as shown in Figure 3b. In the absence of an additive, the CL reaction occurred rapidly whereas in the presence of Zn^{2+}, weak CL emission persisted over several hundred seconds.

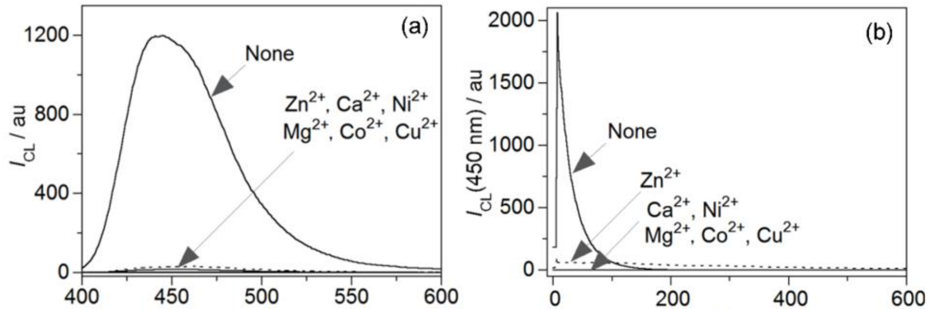


Figure 3. (a) Effects of metal cations (1.0×10^{-2} M) on the CL spectra of cyclic-hydrazide **2** (5.0×10^{-5} M) in DMSO in the presence of H_2O_2 (5.0×10^{-2} M), Bu_4NOH (5.0×10^{-2} M), KI (2.5×10^{-2} M), and metal cations (1.0×10^{-2} M). The CL spectra were recorded 10 s after the CL reaction started. Dotted line shows CL spectrum observed in the presence of Zn^{2+}. (b) Time profiles of the CL of cyclic-hydrazide **2** observed at λ^{CL} 450 nm. Dotted line shows CL profile observed in the presence of Zn^{2+}.

As the spectral profiles of the CL were not apparently altered by concentration of added Zn^{2+} and CL reaction time, relative CL intensity was estimated by integrating the area under the time profile lines of the CL emission. Thus, dependence of the CL intensity on [Zn^{2+}] was investigated as shown in Figure 4. In the absence of an additive, the CL reaction started immediately after addition of the oxidant (H_2O_2 and I_2) and ended within 200 s (Figure 4a). In contrast, in the presence of Zn^{2+} (1.0×10^{-2} M, 200 equiv.), much weaker CL emission was detectable over the longer time domain (> 300 s) compared to the CL emission observed without a metal cation. As seen in Figure 4b, the CL intensity decreased with increased [Zn^{2+}]: 40-equivalents (2×10^{-3} M) of Zn^{2+} completely quenched the CL. The CL responses to Zn^{2+} were not so simple as the effects of Zn^{2+} on the fluorescence of carboximide **1**.

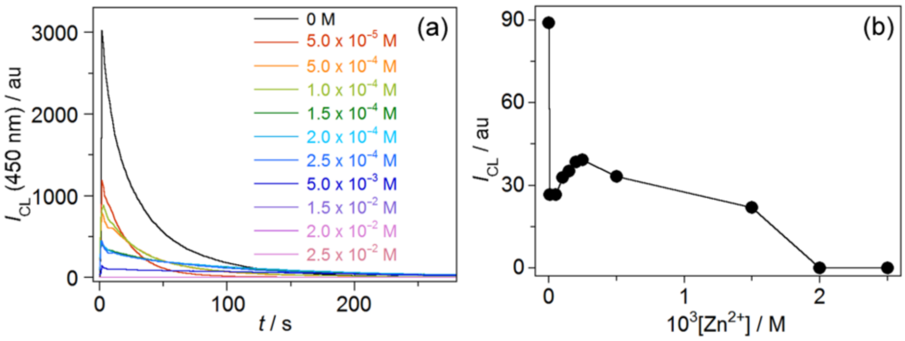


Figure 4. (a) Time profiles of chemiluminescence emission of compound **2** in the presence of Zn^{2+}. (b) Relative CL intensity plotted as a function of [Zn^{2+}]: [**2**] = 5.0×10^{-5} M, [M^{2+}] = 2.0×10^{-2} M, [H_2O_2] = 5.0×10^{-2} M, [Bu_4NOH] = 5.0×10^{-2} M, [KI] = 2.5×10^{-2} M.

Addition of Zn^{2+} displayed opposite effects between the FL of carboximide **1** (off-on) and the CL of cyclic-hydrazide **2** (on-off). In order to reveal detailed effects of Zn^{2+} on the CL reaction of cyclic-hydrazide **2**, absorption and fluorescence spectra of the CL substrate were measured before and after the CL reaction in the presence of Zn^{2+} (Figure 5). The absorption band of cyclic-hydrazide **2** before CL reaction (400–480 nm) slightly red-shifted upon addition of Zn^{2+} (Figure 5a, dotted lines) suggesting that cyclic-hydrazide **2** interacted with Zn^{2+}. After the CL reaction, the original absorption band of cyclic-hydrazide **2** (around 440 nm) vanished and a new absorption band evolved in a shorter wavelength region (360–430 nm, Figure 5a, solid lines). These results indicate that the cyclic-hydrazide **2** was consumed through the CL reaction to form a product (presumably the corresponding dicarboxylate)[19,20] which might display the blue-shifted absorption band compared to the cyclic-hydrazide **2**.

In the presence of Zn^{2+}, because the absorption band of the starting cyclic-hydrazide **2** at *ca*. 440 nm (Figure 5a, dotted red line) disappeared and blue-shifted one was observed in a 370–440 nm wavelength region (Figure 5a, solid red line), it can be considered that Zn^{2+} did not inhibit the chemical reaction of cyclic-hydrazide **2** to produce the CL product. Additionally, the product also interacted with Zn^{2+} because, in the presence of Zn^{2+}, the absorption band of the product mixture red-shifted by 16 nm compared to that observed in the absence of Zn^{2+} (Figure 5(a), compare black and red solid lines).

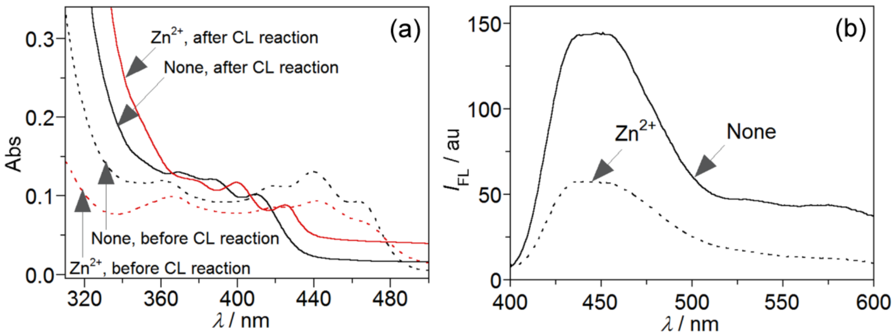


Figure 5. (a) Absorption spectra of the CL mixture of cyclic-hydrazide **2** (5.0×10^{-5} M) in DMSO in the presence H_2O_2 (5.0×10^{-2} M), Bu_4NOH (5.0×10^{-4} M). Dotted lines: Before the CL reaction. Solid lines: After the CL reaction upon addition of KI (2.5×10^{-5} M). (b) Fluorescence spectra (λ_{ex} 350 nm) of the CL reaction mixture of cyclic-hydrazide **2**.

The fluorescence spectra of the CL reaction mixture of cyclic-hydrazide **2** was then measured to get an insight into the effects of Zn^{2+} on the fluorescence properties of the CL product. As shown in Figure 5(b), the CL reaction mixture displayed a similar fluorescence emission band in the wavelength region of 410–520 nm irrespective of the existence of Zn^{2+}. These facts suggest that the interaction between the CL product and Zn^{2+} provided little effect on FL wavelengths of the CL product.

Generally, efficiency of light emission for a CL reaction (Φ_{CL}) is determined by product of yield of the chemical reaction (Φ_R), efficiencies of chemical excitation step (Φ_{EX}) and fluorescence quantum yield of the product (Φ_F) as expressed with eqn 1,

$$\Phi_{CL} = \Phi_R \times \Phi_{EX} \times \Phi_F \quad (1)$$

For the present CL reaction of cyclic-hydrazide **2**, the chemical reaction occurred as seen from the absorption spectral changes before and after the CL reaction ($\Phi_R \neq 0$). Additionally, The CL product displayed fluorescence emission ($\Phi_F \neq 0$). Therefore, Zn^{2+} may affect the chemical excitation step through modification of the Φ_{EX} factor to quench the CL.

SUMMARY

The DPAM-modified carboximide **1** and cyclic-hydrazide **2** were successfully prepared and their emission properties were studied in the presence of metal cations. The fluorescence intensity of carboximide **1** was effectively enhanced by Mg^{2+} and Zn^{2+}. Thus, carboximide **1** serves as an off-on FL probe for these cations as in the case of conventional PET probes. Cyclic-hydrazide **2** displayed blue CL emission upon oxidation with H_2O_2-I_2 mixture in alkaline media. The CL intensity was drastically reduced by addition of metal cations, thus, cyclic-hydrazide **2** displayed on-off response to metal cations. Mg^{2+} and Zn^{2+} effectively quenched the CL emission of cyclic-hydrazide **2** although these cations efficiently enhanced the FL intensity of carboximide **1**. Therefore, it has been demonstrated that these metal cations displayed different effects on the emission behavior between FL of carboximide **1** and CL of cyclic-hydrazide **2**.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were collected on a VARIAN Mercury 300 (300 MHz), a VARIAN VXR-500 (500 MHz) or a VARIAN NMR system 600 MHz (600 MHz) spectrometers. IR spectra were measured using a SHIMADZU IR Prestige-21 spectrophotometer. Electronic absorption spectra were measured using a JASCO V530 spectrophotometer. FL and CL spectra were measured using a HITACHI F2500 spectrofluorophotometer with a 1-cm path-length quartz cell at room temperature under aerated conditions. The spectra were corrected against the instrumental response by using rhodamine B as the standard. The fluorescence quantum yield was determined under aerated conditions by using quinine sulfate (1×10^{-5} M) in 0.5 M sulfuric acid (Φ_F 0.55) [22] as the standard. Spectroscopic grade solvents were used for the absorption and the fluorescence measurements. Perchlorates of Ni^{2+} and Co^{2+}, and trifluoromethanesulfonates of Mg^{2+}, Ca^{2+}, Zn^{2+} and Cu^{2+} were used for the measurements.

9,10-Dimethyl-2,3-anthracenedicarboxylic anhydride 3

Compound **3** was prepared by the previously reported procedure.[21]

9,10-Dimethyl-*N*-propyl-2,3-anthracenedicarboximide 4

A solution of propylamine (0.36 g, 6.1 mmol) in toluene (5 mL) was gradually added to a suspension of anhydride **3** (420 mg, 1.5 mmol) in toluene (250 mL). The mixture was stirred at rt for 30 min, then refluxed for 15 h under a nitrogen atmosphere. After removal of the solvent, the residue was heated in acetic anhydride (60 mL). After removal of acetic anhydride, the residue was purified by silica gel chromatography (CH_2Cl_2/Hexane, 1:1) to afford carboximide **4** (298 mg, 62%). Yellow crystals, mp 251–254 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 1.01 (3H, t, J = 7.5 Hz), 1.79 (2H, sex, J = 7.5 Hz), 3.18 (6H, s), 3.76 (2H, *t*, J = 7.2 Hz), 7.72–7.74 (2H, m), 8.37–8.40 (2H, m), 8.97 (2H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 11.4, 14.7, 21.9, 39.9, 122.8, 125.5, 125.6, 126.8, 130.2, 131.6, 132.8, 168.3. IR (neat) ν_{max}/cm^{-1} 1693, 1752 (CO); UV-vis (MeCN) λ_{max}/nm (log ε) 246 (4.47), 285 (4.48), 298 (4.51), 307 (4.50), 399 (3.79), 421 (3.85). HRMS (FAB): Found *m/z* 317.1388 [M+H]. Calc. for $C_{21}H_{19}NO_2$ 317.1416.

9,10-Bis(bromomethyl)-*N*-propyl-2,3-anthracenedicarboximide 6

A mixture of carboximide **4** (970 mg, 2.94 mmol), *N*-bromosuccinimide (1.4 g, 7.98 mmol), and benzoyl peroxide (138 mg, 0.57 mmol) in CCl_4 (420 mL) was refluxed for 16 h under a nitrogen atmosphere. After removal of the solvent, the residue was washed with MeOH to give dibromide **7** (1.34 g, 96%). Yellow crystals, mp >270 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 1.02 (3H, t, J = 7.5 Hz), 1.80 (2H, sex, J = 7.5 Hz), 3.79 (2H, t, J = 7.3 Hz), 5.51 (4H, s), 7.80–7.84 (2H, m), 8.42–8.45 (2H, m), 8.89 (2H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 11.6, 22.0, 25.6, 40.3, 121.8, 125.0, 127.7, 128.7, 130.5, 131.3, 134.3, 167.8. IR (neat) ν_{max}/cm^{-1} 1260 (CH_2Br), 1698, 1765 (CO). UV-vis (MeCN) λ_{max}/nm (log ε) 241 (4.50), 302 (4.64), 400 (3.94), 423 (3.95). HRMS (FAB): Found *m/z* 473.9704 [M+H]. Calc. for $C_{21}H_{17}Br_2NO_2$ 473.9704.

9,10-Bis[di-(2-picolylamino)methyl]-*N*-propyl-2,3-anthracenedicarboximide 1

To a solution of dibromide **6** (239 mg, 0.50 mmol), and K_2CO_3 (280 mg, 2.0 mmol) in DMF (9 mL) was added dropwise a solution of KI (81 mg, 0.49 mmol) in DMF (4 mL) over 20 min at rt. After stirring for 2 h, the reaction mixture was diluted with 1 M HCl (10 mL) and extracted with AcOEt (2 × 5 mL). The aqueous layer was basified with 4 M NaOH (10 mL), and extracted with AcOEt (2 × 10 mL) and the combined extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on alumina using AcOEt as an eluent to give carboximide **1** (130 mg, 36%). Pale yellow crystals, mp 157–161 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 1.06 (3H, t, J = 7.2 Hz), 1.83 (2H, sex, J = 7.8 Hz), 3.79 (2H, t, J = 7.8 Hz), 3.87 (8H, s), 4.67 (4H, s), 7.08 (4H, dd, J = 5.1, 6.6 Hz), 7.37 (4H, d, J = 7.5 Hz), 7.57–7.60 (2H, m), 7.62 (4H, td, J = 1.8, 7.5 Hz), 8.52–8.55 (2H, m), 9.16 (2H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 11.7, 22.1, 40.1, 51.5, 60.9, 122.3, 123.4, 124.1, 125.7, 126.3, 127.3, 132.2, 133.0, 134.7, 136.7, 149.1, 159.2, 168.4; IR (neat) ν_{max}/cm^{-1} 1709, 1762 (CO). UV-vis (MeCN) λ_{max}/nm (log ε) 245 (4.62), 297 (4.59), 393 (3.81), 415 (4.00). HRMS (FAB): Found *m/z* 712.3406 [M+H]. Calc. for $C_{45}H_{41}N_7O_2$ 712.3400.

6,11-Bis[di-(2-picolylamino)methyl]-naphtho-[2,3-*g*]-2,3-dihydrophthalazine-1,4-dione 2

A solution of carboximide **1** (50.4 mg, 0.07 mmol) and hydrazine hydrate (1.7 g, 35 mmol) in EtOH (5 mL) was refluxed for 21 h. The solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with water and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was washed with acetone to give cyclic-hydrazide **2** (21 mg, 44%). Yellow crystals, mp 225–227 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 3.83 (8H, s), 4.78 (4H, s), 7.05 (4H, dd, J = 4.7 Hz, 7.0 Hz), 7.34 (4H, d, J = 7.7 Hz), 7.55 (4H, td, J = 1.7 Hz, 7.7 Hz), 7.57–7.59 (2H, m), 8.33 (4H, d, J = 4.7 Hz), 8.56–8.57 (2H, m), 9.49 (2H, br s), 11.4 (2H, br s). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 51.4, 60.1, 122.0, 122.9, 125.9, 126.6, 130.9, 132.0, 133.0, 136.3, 148.6, 159. IR (neat) ν_{max}/cm^{-1} 3145 (NH), 1650 (CO). UV-vis (DMSO) λ_{max}/nm (log ε) 360 (3.38), 419 (3.35), 440 (3.42), 463 (3.27). HRMS (FAB): Found *m/z* 685.2997 [M+H]. Calc. for $C_{42}H_{36}N_8O_2$ 685.3039.

Chemiluminescence measurements

To a solution (2 mL) of cyclic-hydrazide **2** (5.0×10^{-5} M), H_2O_2 (5.0×10^{-2} M), Bu_4NOH (5.0×10^{-4} M) and the metal salts (2.0×10^{-2} M) in DMSO was added a solution of KI (200 μL, 2.5×10^{-5} M) in DMSO at rt and the CL spectra were observed using the HITACHI F2500 spectrofluorophotometer.

ACKNOWLEDGEMENTS

The present study was supported by a Grant-in-Aid for Scientific Research, KAKENHI, from JSPS (No. 21550134). HO thanks Prof. Emeritus Jiro Motoyoshiya (Shinshu University) and Prof. Minoru Yamaji (Gunma University) for active discussions and encouragement.

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