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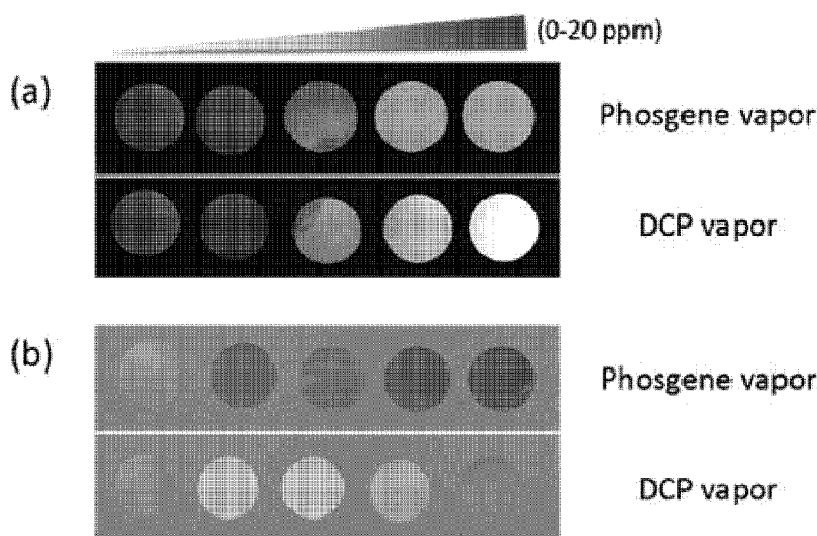
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(54) Title: COMPOUND AND COMPOSITION FOR DETECTING PHOSGENE AND DIETHYL CHLOROPHOSPHATE



(57) Abstract: The present invention relates to a compound for detecting phosgene and DCP (diethyl chlorophosphate) and a composition for detecting phosgene and DCP (diethyl chlorophosphate) comprising the said compound. More precisely, the compound for detecting phosgene and DCP of the present invention can selectively detect phosgene and DCP either in the liquid phase of gas phase by detecting the changes of fluorescence and color development very quickly within a few seconds with nM sensitivity. Therefore, the compound can also be effectively used as an ingredient for the composition and kit for the detection of one or more materials selected from the group consisting of phosgene and DCP.

Description

Title of Invention: COMPOUND AND COMPOSITION FOR DETECTING PHOSGENE AND DIETHYL CHLOROPHOSPHATE

Technical Field

[1] The present invention relates to a compound and a composition for detecting phosgene and DCP (diethyl chlorophosphate).

[2]

Background Art

[3] Phosgene is a highly toxic gas which is colorless at room temperature. Phosgene sits in top 10% of the most toxic materials. It has also been known as a notorious chemical warfare agent (CWA) since it killed more than 100,000 people as a chemical weapon during World War I.

[4] Once exposed on phosgene, the respiratory system is severely damaged, leading to the disease such as noncardiogenic pulmonary edema and emphysema and even death. Unlike other chemical warfare agents such as Sarin, Soman, Taburn, and DCP (diethyl chlorophosphate), phosgene has a latent period with no apparent symptoms, during which pulmonary edema is developed due to its unique toxicity that leads to death.

[5]

[6] There is no method to detect patients exposed on phosgene at the latent stage or to determine the possibility of the development of pulmonary edema thereby. The production of Sarin, Soman, and Taburn is limited by law but phosgene is widely used in industry and used as a starting material for the production of other compounds, insecticides, pharmaceuticals and isocyanate-based polymers. Therefore, there is a relatively high chance of a disaster occurring due to the exposure by an accident or other routes.

[7] So, human lives can be damaged or lost by intentionally induced exposure on phosgene through war or terror or massive civil damage can be induced by the exposure through an industrial accident, making phosgene a highly dangerous material.

[8] Therefore, it is very important to detect phosgene fast and accurately for protecting human lives. It is also necessary to develop a method to detect phosgene selectively from other gases or CWAs.

[9]

[10] Sensors are under development to detect CWA by detecting the changes of fluorescence or color development (Santu Sarkar and Raja Shunmugam. Chem. Commun., 2014, 50, 8511-8513). It is still requested to develop a fluorescent chemical sensor or

color sensor to detect CWA faster and more sensitively within a few seconds. Moreover, a sensor to detect a target material from other CWAs or gases has not been developed yet.

[11]

[12] Thus, the present inventors have been studied to develop a method to detect phosgene selectively fast and accurately within a few seconds by detecting the changes of fluorescence or color development. In the course of the study, the present inventors confirmed that the compound of the present invention can detect phosgene and DCP (diethyl chlorophosphate) fast and accurately within a few seconds at even nM unit by screening the changes of fluorescence and color development and can detect phosgene and DCP selectively from other CWAs or gases, leading to the completion of the present invention.

[13]

Disclosure of Invention

Technical Problem

[14] It is an object of the present invention to provide a compound for detecting phosgene and DCP (diethyl chlorophosphate).

[15] It is another object of the present invention to provide a method for the preparation of the compound above.

[16] It is also an object of the present invention to provide a composition for detecting phosgene comprising the said compound above.

[17] It is further an object of the present invention to provide a composition for the detection of DCP (diethyl chlorophosphate) comprising the said compound above.

[18] It is also an object of the present invention to provide a kit for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) which comprises the said compound above.

[19] It is also an object of the present invention to provide a method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) by using the detection kit above.

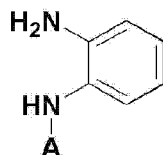
[20]

Solution to Problem

[21] To achieve the above objects, the present invention provides a compound represented by formula 1 below.

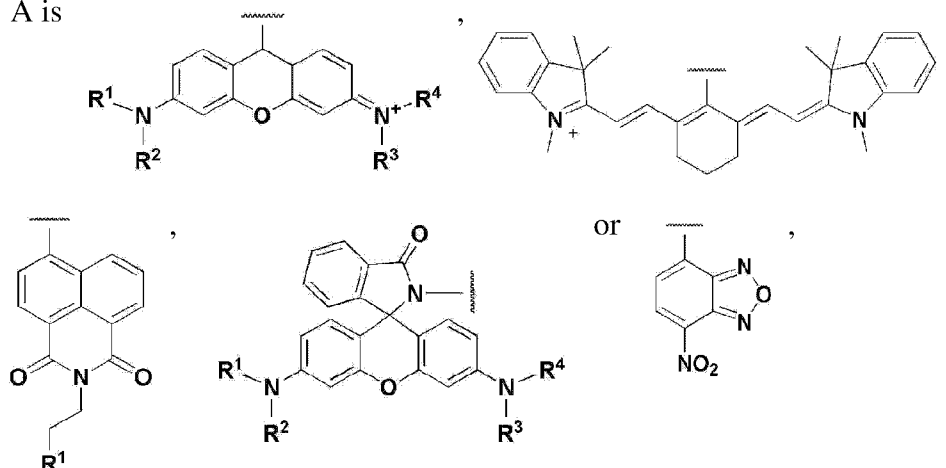
[22] [Formula 1]

[23]



[24] In the formula 1,

[25] A is



[26] R^1 is -H, C_{1-10} straight or branched alkyl, C_{1-10} straight or branched alkoxy, or 4-7 membered heterocycloalkyl containing 1-3 hetero atoms selected from the group consisting of N, O, and S; and

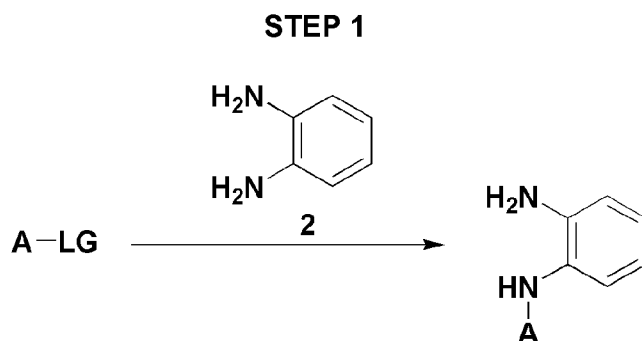
[27] R^2 , R^3 and R^4 is independently -H, C_{1-10} straight or branched alkyl, or C_{1-10} straight or branched alkoxy.

[28]

[29] The present invention also provides a method for preparing the compound represented by formula 1 containing the step of reacting the compound represented by A-LG with the compound represented by formula 2 to give the compound represented by formula 1 (step 1) as shown in the below reaction formula 1.

[30] [Reaction Formula 1]

[31]



[32] In the reaction formula 1, A is as defined in formula 1 of claim 1; and

[33] LG is =O, =S or halogene.

[34] Further, the present invention provides a composition for detecting phosgene comprising the compound represented by formula 1.

[35] The present invention also provides a composition for the detection of DCP (diethyl chlorophosphate) comprising the compound represented by formula 1.

[36] The present invention also provides a kit for the detection of one or more compounds

selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) comprising the compound represented by formula 1.

- [37] The present invention also provides a method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) comprising the following steps:
- [38] contacting the detection kit of the invention with the sample to be analyzed (step 1); and
- [39] evaluating the changes of fluorescence or absorption properties of the compound represented by formula 1 included in the detection kit after the contact of step 1 (step 2).

[40]

Advantageous Effects of Invention

- [41] The compound for detecting phosgene and DCP (diethyl chlorophosphate) of the present invention can selectively detect phosgene and DCP (diethyl chlorophosphate) either in the liquid phase or gas phase by detecting the changes of fluorescence and color development very quickly within a few seconds with nM sensitivity. Therefore, the compound can be effectively used as a composition for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate).

[42]

Brief Description of Drawings

- [43] The application of the preferred embodiments of the present invention is best understood with reference to the accompanying drawings, wherein:
- [44] Figure 1(a) is a graph illustrating the fluorescence spectrum of the compound of example 1 of the invention according to the concentration of phosgene.
- [45] Figure 1(b) is a graph illustrating the absorption spectrum of the compound of example 1 of the invention according to the concentration of phosgene.
- [46] Figure 2(a) is a graph illustrating the fluorescence spectrum of the compound of example 1 of the invention according to the concentration of DCP (diethyl chlorophosphate).
- [47] Figure 2(b) is a graph illustrating the absorption spectrum of the compound of example 1 of the invention according to the concentration of DCP (diethyl chlorophosphate).
- [48] Figure 3(a) is an image illustrating the changes of fluorescence resulted from the exposure on gas-phase phosgene or gas-phase DCP (diethyl chlorophosphate). Precisely, the compound of example 1 was prepared as a sensor which was exposed on gas-phase phosgene or gas-phase DCP, followed by observation of the changes of fluorescence in there.

- [49] Figure 3(b) is an image illustrating the changes of color development resulted from the exposure on gas-phase phosgene or gas-phase DCP (diethyl chlorophosphate). Precisely, the compound of example 1 was prepared as a sensor which was exposed on gas-phase phosgene or gas-phase DCP, followed by observation of the changes of color development in there.
- [50] Figure 4 is a photograph illustrating the experimental step to contact the filter-paper retaining the compound of example 2 with 0.8 mg/L of phosgene.
- [51] Figure 5 is a photograph illustrating the experimental step to contact the filter-paper retaining the compound of example 2 with 8 mg/L of phosgene.
- [52] Figure 6 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 without the exposure on phosgene, photographed at 365 nm.
- [53] Figure 7 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 and exposed on 0.8 mg/L of phosgene, photographed at 365 nm.
- [54] Figure 8 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 and exposed on 8 mg/L of phosgene, photographed at 365 nm.
- [55] Figure 9 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 without the exposure on phosgene, photographed at 365 nm.
- [56] Figure 10 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 which was exposed on 0.8 mg/L of phosgene, photographed at 365 nm.
- [57] Figure 11 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 which was exposed on 8 mg/L of phosgene, photographed at 365 nm.
- [58] Figure 12 is photographs illustrating the fluorescence characteristics of the silica gel containing the compound of example 2 after the treatment of 0(a), 3(b) and 30(c) μ g triphosgene.
- [59] Figure 13(a) is a graph illustrating the fluorescence spectrum of the compound of example 2 of the invention according to the concentration of phosgene.
- [60] Figure 13(b) is a graph illustrating the absorption spectrum of the compound of example 2 of the invention according to the concentration of phosgene.

[61]

Best Mode for Carrying out the Invention

- [62] Practical and presently preferred embodiments of the present invention are illustrative as shown in the following Examples.

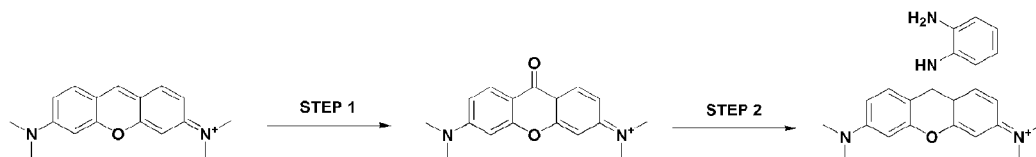
- [63] However, it will be appreciated that those skilled in the art, on consideration of this

disclosure, may make modifications and improvements within the spirit and scope of the present invention.

[64]

[65] <Preparative Example 1> Preparation of o-phenylenediamine-pyronine(N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium)

[66]



[67] Step 1: Preparation of N-(6-(dimethylamino)-9-oxo-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[68] N-(6-(dimethylamino)-3H-xandene-3-ylidene)-N-methylmethanaminium was reacted with KCN for 18 hours, reacted with FeCl₃/HCl for 12 hours, and then reacted with NaHCO₃, resulting in the preparation of N-(6-(dimethylamino)-9-oxo-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium.

[69]

[70] Step 2: Preparation of N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[71] The compound prepared in step 1 above was reacted with Tf₂O and then reacted with benzene-1,2-diamine to give N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium (yield: 40%).

[72]

[73] <Example 1> Preparation of Compounds for Detecting Phosgene and DCP 1

[74] Step 1: Preparation of N-(6-(dimethylamino)-9-thioxo-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[75]



[76] THF (40 ml) containing t-BuOK (0.56 g, 3 eq) was added to the solution containing Pyronine Y (N-(6-(dimethylamino)-3H-xandene-3-ylidene)-N-methylmethanaminium) (0.5 g, 1.65 mmol) and sulfur (0.79 g, 15 eq). The reaction mixture was refluxed for 10 hours. Termination of the reaction was confirmed by TLC. Then, the reaction mixture was cooled down at room temperature and filtered. Silica gel column chromatography was performed with the residue (eluent, PE:DCM, 1:1) to give the target

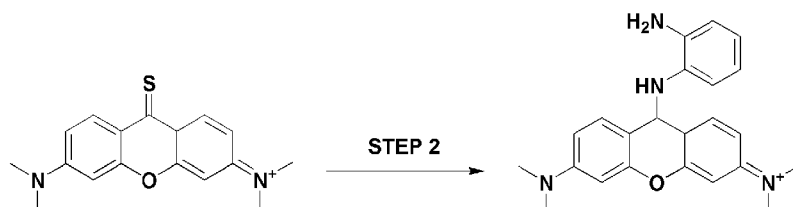
compound as a yellow solid (yield: 50%).

[77] ^1H NMR (300 MHz, CDCl_3), δ : 8.70 (d, J = 9.2 Hz, 2H), 6.75 (dd, J = 9.2, 2.3 Hz, 2H), 6.43 (d, J = 2.3 Hz, 2H), 3.13 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3), δ : 196.26, 154.58, 153.03, 131.80, 120.07, 110.52, 96.06, 40.24. ESI-MS: Calcd. for 299.11; Found 299.20.

[78]

[79] Step 2: Preparation of N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[80]



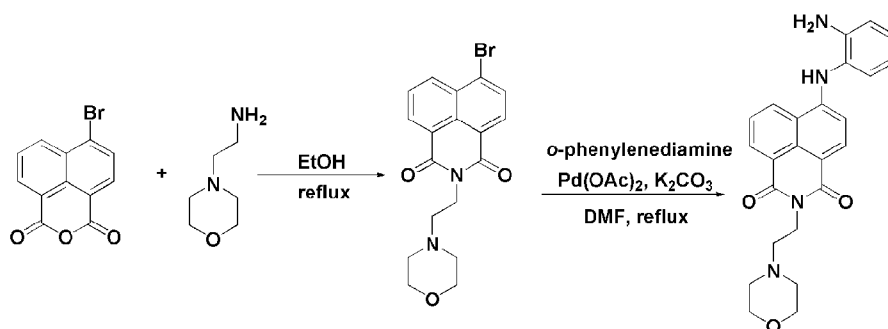
[81] 90 μl (2 eq) of Tf_2O was added drop by drop to the anhydrous CH_2Cl_2 solution (10 ml) containing 80 mg (0.268 mmol) of the compound prepared in step 1 above dissolved therein. The reaction mixture was well mixed with stirring at room temperature for 10 minutes. 0.29 g (10 eq) of o-phenylenediamine solution was added to the reaction mixture above, followed by stirring for 10 more hours. Then, CH_2Cl_2 was eliminated under reduced pressure. The solid residue was purified by silica gel chromatography (eluent, EA:DCM, 1:2) to give the target compound as a yellow solid (yield: 80%).

[82] ^1H NMR (300 MHz, MeOD), δ : 7.78 (d, J = 9.5 Hz, 2H), 7.25 (m, 1H), 7.09 (dd, J = 7.8, 1.4 Hz, 1H), 6.96 (dd, J = 7.8, 1.4 Hz, 1H), 6.81 (dd, J = 3.9, 1.9 Hz, 1H), 6.76 (m, 2H), 6.71 (d, J = 2.5 Hz, 2H), 3.18 (s, 12H). ^{13}C NMR (75 MHz, MeOD), δ : 157.01, 155.46, 154.03, 147.21, 143.91, 129.31, 126.98, 126.52, 117.72, 116.26, 110.67, 102.83, 96.68, 38.80. ESI-MS: $[\text{M}]^+$ Calcd. for 372.20; Found 372.30.

[83]

[84] <Example 2> Preparation of Compounds for Detecting Phosgene and DCP 2

[85]



[86] To a solution of 4-bromo-1,8-naphthalene anhydride (1.38 g, 5.0 mmol) in anhydrous EtOH (20.0 ml) at room temperature was added 4-(2-aminoethyl)morpholine (715 mg,

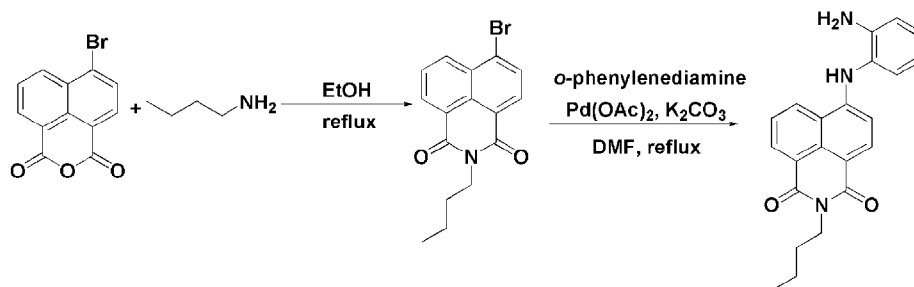
5.5 mmol). After refluxing for 4 h, the reaction mixture was cooled and filtered to give 4-bromine-1,8-naphthalimide. This naphthalimide(389 mg, 1.0 mmol) and o-phenylenediamine(540 mg, 5.0 mmol) were dissolved in anhydrous DMF (20 mL), Subsequently, K₂CO₃ (550 mg, 4 mmol) and Pd(OAc)₂ (44 mg, 2 mmol) was added under nitrogen. The reaction was then refluxed overnight. The solvent DMF was then removed under vacuum. The crude product was treated with water, extracted with dichloromethane and dried over anhydrous MgSO₄. The organic layer was removed and the residue was purified by column chromatography to give 0.18 g of product (yellow solid, 43%).

- [87] ¹H NMR (CDCl₃, 300MHz) δ (ppm) = 8.59 (m, 1H), 8.35 (d, 1H), 8.28 (d, 1H), 7.69 (m, 1H), 7.17 (m, 2H), 6.92-6.77 (m, 2H), 6.67 (d, 1H), 6.53 (s, 1H), 4.37-4.23 (m, 2H), 3.79 (s, 2H), 3.71-3.88 (m, 4H), 2.72-2.61, 2H), 2.57 (s, 4H). ¹³C NMR (75 MHz, CDCl₃) δ = 164.51, 163.89, 147.49, 142.82, 133.96, 131.31, 128.32, 127.44, 126.22, 125.32, 124.50, 123.21, 120.74, 119.50, 116.75, 112.30, 107.75, 67.02, 56.23, 53.80, 36.98. HRMS (ESI) m/z = 417.1718 [M + H]⁺, calcd for C₂₄H₂₅N₄O₃=417.1927.

[88]

[89] <Example 3> Preparation of Compounds for Detecting Phosgene and DCP 3

[90]



- [91] To a solution of 4-bromo-1,8-naphthalene anhydride (1.38 g, 5.0 mmol) in anhydrous EtOH (20.0 ml) was added butylamine (480 mg, 5.5 mmol) at room temperature. After refluxing for 4 h, the reaction mixture was cooled and filtered to give 4-bromine-1,8-naphthalimide. This naphthalimide (540 mg, 5.0 mmol) and o-phenylenediamine(540 mg, 5.0 mmol) were dissolved in anhydrous DMF (20 mL), Subsequently, K₂CO₃ (550 mg, 4 mmol) and Pd(OAc)₂ (44 mg, 2 mmol) under nitrogen. The reaction was then refluxed overnight. The solvent DMF was then removed under vacuum. The crude product was treated with water, extracted with dichloromethane and dried over anhydrous MgSO₄. The organic layer was removed and the residue was purified by column chromatography to give 0.11 g of product (yellow solid, 61%).

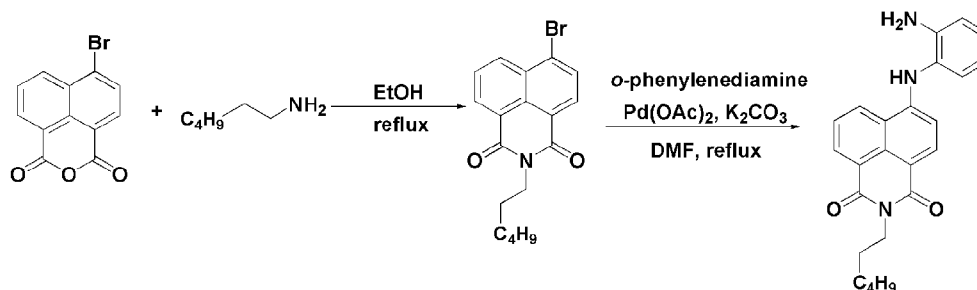
- [92] ¹H NMR (DMSO-d₆, 300MHz) δ (ppm) = 9.01 (s, 1H), 8.91-8.88 (m, 1H), 8.50-8.47 (m, 1H), 8.20 (d, J = 8.6Hz, 1H), 7.78-7.73 (m, 1H), 7.09 (t, J = 7.2Hz, 2H), 6.88-6.84 (m, 1H), 6.69-6.63 (m, 1H), 6.41 (d, J = 8.5Hz, 1H), 5.04 (s, 2H), 4.16-3.89 (m, 2H),

1.58 (d, $J = 7.5\text{Hz}$, 2H), 1.47-1.19 (m, 2H), 0.92 (t, $J = 7.3\text{Hz}$, 3H); ^{13}C NMR DMSO- d_6 , $\delta = 164.47, 163.63, 150.48, 145.65, 134.54, 131.47, 130.23, 130.05, 128.82, 128.44, 125.14, 123.99, 122.55, 121.34, 117.19, 116.35, 109.79, 107.01, 55.61, 30.53, 20.51, 14.46$. HRMS (ESI) $m/z = 360.1706$ $[\text{M} + \text{H}]^+$, calcd for $\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_3 = 360.1712$.

[93]

[94] <Example 4> Preparation of Compounds for Detecting Phosgene and DCP 4

[95]

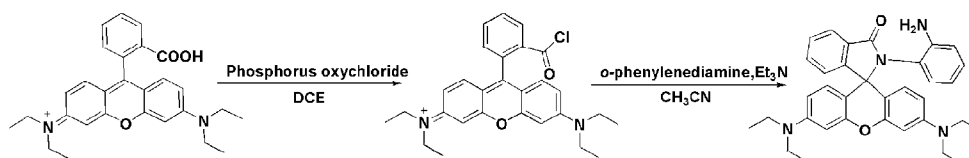


[96] The target compound was prepared by conducting the same synthesis as in Example 3 except that hexylamine was used instead of the butylamine used in Example 3.

[97]

[98] <Example 5> Preparation of Compounds for Detecting Phosgene and DCP 5

[99]



[100] To a solution of rhodamine B base (1.01 g, 2.3 mmol) in dry 1,2-dichloroethane (8.0 mL) at room temperature was added phosphorus oxychloride (6.9 mmol) over a period of 5 min. After being stirred at reflux for 4 h, the mixture was cooled and concentrated under vacuum to give the crude rhodamine B acid chloride. A solution of the acid chloride in dry acetonitrile (10 mL) was added dropwise to a solution of o-diaminobenzene (14 mmol) in dry acetonitrile (6.0 mL) containing triethylamine (8.0 mL). After being stirred for 4 h at room temperature, the mixture was concentrated under vacuum, and the residue was subjected to column chromatography to give target compound as a white solid in 83% yield.

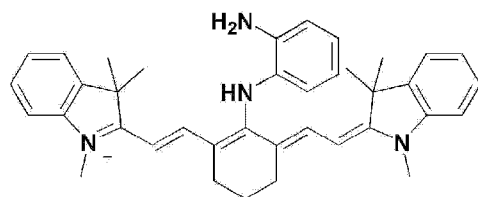
[101] ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 8.03-8.05 (m, 1H); 7.53-7.60 (m, 2H); 7.25-7.27 (m, 1H); 6.94 - 6.99 (m, 1H); 6.68 (d, $J = 8.7\text{Hz}$, 2H); 6.58 (dd, $J = 7.8\text{Hz}$, $J = 1.2\text{Hz}$, 1H); 6.40-6.46 (m, 1H); 6.31 (d, $J = 8.7\text{Hz}$, 2H); 6.28 (b, 2H); 6.10 (dd, $J = 8.1\text{Hz}$, $J = 1.5\text{Hz}$, 1H); 3.44 (s, 2H); 3.35 (q, $J = 6.9\text{Hz}$, 8H); 1.16 (t, $J = 7.2\text{Hz}$, 12H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 166.63, 161.22, 154.20, 152.66, 149.15, 144.75, 132.81, 129.03, 128.97, 128.85, 128.55, 124.51, 123.66, 122.46, 118.43, 117.23,

108.21, 98.28, 68.27, 44.60, 31.15, 12.76. HRMS (ESI) m/z calcd for $C_{34}H_{36}N_4O_2$ $[M + H]^+$ 533.2565. Found 533.2838.

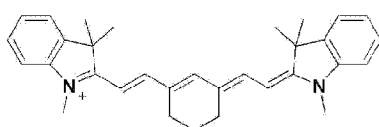
[102]

[103] <Example 6> Preparation of Compounds for Detecting Phosgene and DCP 6

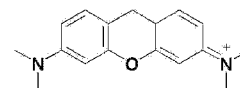
[104]



[105] The target compound was prepared by carrying out the same synthesis as in Example 1 except that



was used instead of

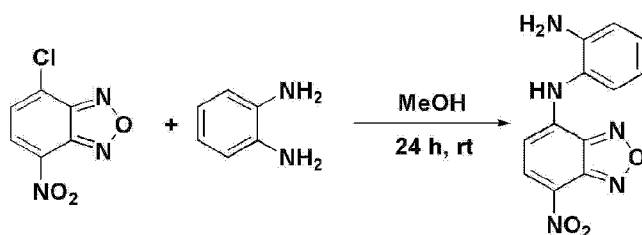


in the step 1 of Example 1 above.

[106]

[107] <Example 7> Preparation of Compounds for Detecting Phosgene and DCP 7

[108]



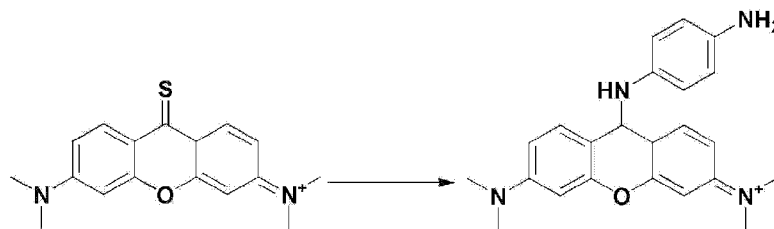
[109] To a solution of o-phenylenediamine (0.32 g, 3.0 mmol) in methanol (10 mL) was added NBD-Cl (0.20 g, 1.0 mmol) in methanol (10 mL) at room temperature with stirring. The resulting mixture was stirred at room temperature for 24 hours. Filtered and washed several times with methanol to give a target compound (reddish brown solid, 71%).

[110] 1H NMR (DMSO- d_6 , 300 MHz) : δ 10.69 (brs, 1H), 8.54 (d, J = 8.7 Hz, 1H), 7.09-7.15 (m, 2H), 6.84 (d, J = 7.2 Hz, 1H), 6.64 (t, J = 7.8 Hz, 1H), 5.93 (d, J = 8.7 Hz, 1H), 5.27 (brs, 2H). ^{13}C NMR (DMSO- d_6 , 75 MHz) : δ 145.49, 145.04, 144.96, 144.92, 138.58, 129.44, 128.14, 121.95, 116.77, 116.49, 113.59, 102.34. HRMS (EI) m/z = 270.0640 $[M]^+$, calcd for $C_{12}H_9N_5O_3$ = 270.0704.

[111]

[112] <Comparative Example 1> Preparation of N-(9-(4-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[113]



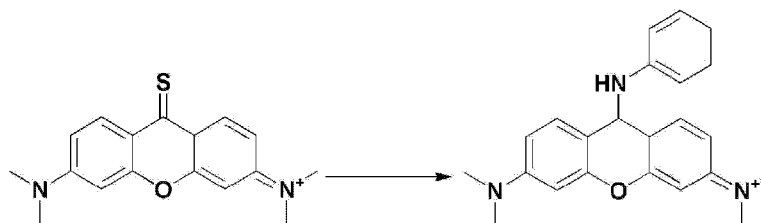
[114] 50 mg (0.168 m mol) of the compound prepared in step 1 of example 1 was dissolved in CH_2Cl_2 (10 ml), to which 57 μl (2 eq) of Tf_2O was added drop by drop. The reaction mixture was stirred for 10 minutes, to which 235 μl (15 eq) of phenylamine was added. The mixture was stirred at room temperature for overnight. Upon completion of the reaction, CH_2Cl_2 was eliminated under reduced pressure. The solid residue was purified by silica gel chromatography (eluent, EA:DCM, 1:3) to give the target compound as an orange solid (yield: 70%).

[115] ^1H NMR (300 MHz, MeOD), δ : 7.67 (d, J = 9.5 Hz, 2H), 7.56 (dd, J = 7.7, 6.6 Hz, 2H), 7.46 (m, 1H), 7.40 (d, J = 7.7 Hz, 2H), 6.80 (dd, J = 9.5, 2.4 Hz, 2H), 6.73 (d, J = 2.4 Hz, 2H), 3.19 (s, 12H). ^{13}C NMR (75 MHz, MeOD), δ : 157.34, 155.65, 153.33, 140.66, 129.94, 127.66, 127.16, 125.05, 110.83, 102.73, 96.32, 38.86. ESI-MS: $[\text{M}]^+$ Calcd for 358.19; Found 358.30.

[116]

[117] <Comparative Example 2> Preparation of N-(6-(dimethylamino)-9-(phenylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[118]



[119] 100 mg (0.336 m mol) of the compound prepared in step 1 of example 1 was dissolved in CH_2Cl_2 (15 ml), to which 114 μl (2 eq) of Tf_2O was added drop by drop. The reaction mixture was stirred for 10 minutes, to which 0.54 g (15 eq) of p-phenylenediamine was added. The mixture was stirred at room temperature for overnight. Upon completion of the reaction, the solvent was eliminated under reduced pressure. The solid residue was purified by silica gel chromatography (eluent, DCM:EtOH, 30:1) to give the target compound as a yellow solid (yield: 70%).

[120] ^1H NMR (300 MHz, MeOD) δ 7.74 (s, 2H), 7.13 (m, 2H), 6.84 (m, 4H), 6.70 (d, J = 2.5 Hz, 2H), 3.18 (s, 12H). ^{13}C NMR (75 MHz, MeOD) δ 157.01, 154.99, 150.34, 129.75, 128.51, 127.92, 116.80, 112.16, 103.60, 97.75, 40.26. $[\text{M}]^+$ calcd for 373.20, Found 373.30.

[121]

[122] <Experimental Example 1> Evaluation of phosgene detection ability of the compound of example 1

[123] The following experiment was performed in order to evaluate the phosgene detection ability of the compound prepared in example 1.

[124] Particularly for the safety of the experiment, non-volatile and relatively less toxic triphosgene, the precursor of phosgene, was used instead of the volatile phosgene to evaluate the detection ability of the compound prepared in example 1. The compound of example 1 was loaded in chloroform at the concentration of 10 μ M, to which triphosgene was added with different concentrations (0-2 eq), during which the changes of fluorescence and absorbance were observed to evaluate the phosgene detection ability. The results are shown in Figure 1. In the experiment, excitation wavelength was 580 nm and slit width was 1.5 nm. Each spectrum was measured at 2 min intervals.

[125] Figure 1(a) is a graph illustrating the fluorescence spectrum of the compound of example 1 of the invention according to the concentration of phosgene, wherein the fluorescence photograph is on the right side of the graph. Figure 1(b) is a graph illustrating the absorption spectrum of the compound of example 1 of the invention according to the concentration of phosgene, wherein the color development photograph is on the right side of the graph.

[126] As shown in Figure 1(a), the fluorescence intensity of the compound of example 1 of the invention was stronger as the concentration of phosgene was increased, and thus red fluorescence was observed with the naked eye. As shown in Figure 1(b), wavelength band of the absorption spectrum of the compound of example 1 of the invention was changed as the concentration of phosgene was increased. The color thereof started yellow and turned purple, which was also observed with the naked eye.

[127] Therefore, the compound for detecting phosgene of the present invention can be effectively used as a composition for detecting phosgene since the changes of fluorescence and color development can be observed with the naked eye.

[128]

[129] <Experimental Example 2> Evaluation of DCP (diethyl chlorophosphate) detection ability of the compound of example 1

[130] The following experiment was performed by the same manner as described in experimental example 1 in order to evaluate the DCP detection ability of the compound prepared in example 1 of the invention except that DCP (diethyl chlorophosphate) was used instead of phosgene. The results are shown in Figure 2.

[131] Figure 2(a) is a graph illustrating the fluorescence spectrum of the compound of example 1 of the invention according to the concentration of DCP (diethyl

chlorophosphate), wherein the fluorescence photograph is on the right side of the graph.

[132] Figure 2(b) is a graph illustrating the absorption spectrum of the compound of example 1 of the invention according to the concentration of DCP (diethyl chlorophosphate).

[133] As shown in Figure 2(a), the fluorescence intensity of the compound of example 1 of the invention was stronger as the concentration of DCP (diethyl chlorophosphate) was increased, and thus green fluorescence was observed with the naked eye.

[134] As shown in Figure 2(b), wavelength band of the absorption spectrum of the compound of example 1 of the invention was changed as the concentration of DCP (diethyl chlorophosphate) was increased.

[135] Therefore, the compound for the detection of DCP (diethyl chlorophosphate) of the present invention can be effectively used as a composition for the detection of DCP (diethyl chlorophosphate) since the changes of fluorescence and color development can be observed with the naked eye.

[136]

[137] <Experimental Example 3> Evaluation of gas-phase phosgene and DCP (diethyl chlorophosphate) detection ability of the compound of example 1

[138] The following experiment was performed in order to evaluate the gas-phase phosgene and DCP detection ability of the compound of example 1 of the invention.

[139] Particularly, in order to evaluate whether or not the compound prepared in example 1 could act as a real sensor to detect gas-phase phosgene and DPC efficiently, a kit was constructed wherein the compound of example 1 was fixed on polyethylene oxide film. The kit was exposed on different concentrations of phosgene and DCP (0-20 ppm), followed by observation of the changes of fluorescence and color development in the compound of example 1. The results are shown in Figure 3.

[140] Figure 3(a) is an image illustrating the changes of fluorescence resulted from the exposure on gas-phase phosgene or gas-phase DCP (diethyl chlorophosphate). Precisely, the compound of example 1 was prepared as a sensor which was exposed on gas-phase phosgene or gas-phase DCP, followed by observation of the changes of fluorescence.

[141] Figure 3(b) is an image illustrating the changes of color development resulted from the exposure on gas-phase phosgene or gas-phase DCP (diethyl chlorophosphate). Precisely, the compound of example 1 was prepared as a sensor which was exposed on gas-phase phosgene or gas-phase DCP, followed by observation of the changes of color development.

[142] As shown in Figure 3, the compound of the example of the present invention can be useful as a sensor to detect the changes of fluorescence and color development

according to the exposure on gas-phase phosgene and DCP (diethyl chlorophosphate).

[143]

[144] <Experimental Example 4> Evaluation 1 of phosgene detection ability of the compound of example 2

[145] The following experiment was performed to evaluate whether or not the compound of example 2 was useful for the detection of gas-phase phosgene.

[146] A filter paper was cut into 2 cm x 1 cm and dipped in DCM solution (1 mg/mL) containing the compound of example 2 dissolved therein. The filter paper was dried to eliminate the solvent. Then, the filter paper was placed in a sealed flask containing 0.2 mg of phenanthridine and 0.2 mg of triphosgene. The concentration of phosgene therein was 0.8 mg/L (Figure 4) or 8 mg/L (Figure 5). The filter paper, exposed or not exposed on 0.8 mg/L or 8 mg/L of phosgene, was photographed at 365 nm (Figures 6 ~ 8).

[147] Figure 4 is a photograph illustrating the experimental step to contact the filter-paper retaining the compound of example 2 with 0.8 mg/L of phosgene.

[148] Figure 5 is a photograph illustrating the experimental step to contact the filter-paper retaining the compound of example 2 with 8 mg/L of phosgene.

[149] Figure 6 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 without the exposure on phosgene, photographed at 365 nm.

[150] Figure 7 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 and exposed on 0.8 mg/L of phosgene, photographed at 365 nm.

[151] Figure 8 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 and exposed on 8 mg/L of phosgene, photographed at 365 nm.

[152] As shown in Figures 6 ~ 8, fluorescence properties of the filter-paper retaining the compound of example 2 exposed on phosgene were changed(Figure 7(fluorescence, green) and Figure 8(fluorescence, cyan(Stronger fluorescence than Figure 7))), compared with the glass plate coated with the compound of example 2 not-exposed on phosgene(Figure 9(no fluorescence, black)).

[153] Therefore, it was confirmed that gas-phase phosgene could be easily detected by using the compound of example 2 with the naked eye.

[154]

[155] <Experimental Example 5> Evaluation 2 of phosgene detection ability of the compound of example 2

[156] The following experiment was performed to evaluate whether or not the compound of example 2 was useful for the detection of gas-phase phosgene.

[157] The gas-phase phosgene detection ability of the compound of example 2 was evaluated by the same manner as described in example 4 except that a thin glass plate

was used. The results are shown in Figures 9 ~ 11.

[158] Figure 9 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 without the exposure on phosgene, photographed at 365 nm.

[159] Figure 10 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 which was exposed on 0.8 mg/L of phosgene, photographed at 365 nm.

[160] Figure 11 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 which was exposed on 8 mg/L of phosgene, photographed at 365 nm.

[161] As shown in Figures 9 ~ 11, fluorescence properties of the glass plate coated with the compound of example 2 exposed on phosgene were changed(Figure 10(fluorescence, dark blue) and Figure 11(fluorescence, blue(Stronger fluorescence than Figure 10)), compared with the filter-paper retaining the compound of example 2 not-exposed on phosgene(Figure 9(no fluorescence, black)).

[162] Therefore, it was confirmed that the compound of example 2 of the invention is effective in detecting gas-phase phosgene by observing the changes of fluorescence properties.

[163]

[164] <Experimental Example 6> Evaluation 3 of phosgene detection ability of the compound of example 2

[165] The following experiment was performed to evaluate whether or not the compound of example 2 was useful for the detection of liquid-phase phosgene.

[166] 30 µg of the compound of example was absorbed in 30 mg of silica gel, which was treated with 3 µg or 30 µg of triphosgene dissolved in chloroform. Then, the changes of fluorescence properties were observed and one of the results is presented in Figure 12.

[167] Figure 12 is photographs illustrating the fluorescence characteristics of the silica gel containing the compound of example 2 after the treatment of 0(a), 3(b) and 30(c) µg triphosgene.

[168] As shown in Figure 12, fluorescence properties of the silica gel retaining the compound of example 2 treated with phosgene(b and c) were changed, compared with the silica gel retaining the compound of example 2 not-treated with phosgene(a).

[169] Therefore, it was confirmed that the compound of example 2 of the invention is effective in detecting liquid-phase phosgene by observing the changes of fluorescence properties.

[170]

[171] <Experimental Example 7> Evaluation 4 of phosgene detection ability of the

compound of example 2

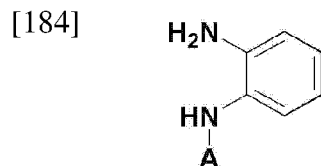
- [172] The following experiment was performed in order to evaluate the phosgene detection ability of the compound prepared in example 2.
- [173] Particularly for the safety of the experiment, non-volatile and relatively less toxic triphosgene, the precursor of phosgene, was used instead of the volatile phosgene to evaluate the detection ability of the compound prepared in example 2. Ex wavelength = 340 nm, slit width = 5*3; Probe (10 um) with different equivalent of Triphosgene in p-Xylene as solvent with 1 % chloroform as the co-solvent. The results are shown in Figure 13. Each spectrum was measured at 2 min intervals.
- [174] Figure 13(a) is a graph illustrating the fluorescence spectrum of the compound of example 2 of the invention according to the concentration of phosgene. Figure 13(b) is a graph illustrating the absorption spectrum of the compound of example 2 of the invention according to the concentration of phosgene.
- [175] As shown in Figure 13(a), the fluorescence intensity of the compound of example 2 of the invention was stronger as the concentration of phosgene was increased. As shown in Figure 13(b), wavelength band of the absorption spectrum of the compound of example 2 of the invention was changed as the concentration of phosgene was increased.
- [176] Therefore, the compound for detecting phosgene of the present invention can be effectively used as a composition for detecting phosgene since the changes of fluorescence and color development can be observed.
- [177]
- [178] In the above Experimental Examples 1-7, it was found that the compounds according to the present invention react with phosgene or DCP in a gaseous or liquid state to induce changes in fluorescence and color development at nM concentration, which induces different changes according to whether it is a phosgene or a DCP. Accordingly, the compounds of the invention or compositions containing the same may be usefully employed for phosgene and DCP detection, And can be used in the entire industry as a detection composition and a kit which are capable of selectively detecting and sensitively detecting to exposure of phosgene and DCP.

[179]

Mode for the Invention

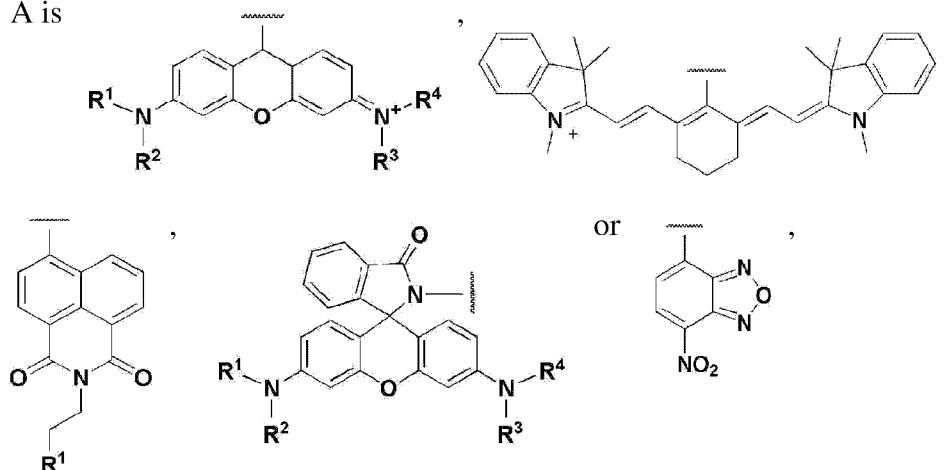
- [180] Hereinafter, the present invention is described in detail. It is to be understood, however, that the following description is provided to assist the understanding of the present invention, and the present invention is not limited thereto.
- [181]
- [182] The present invention provides a compound represented by formula 1 below.

[183] [Formula 1]



[185] In the formula 1,

[186] A is



[187] R¹ is -H, C₁₋₁₀ straight or branched alkyl, C₁₋₁₀ straight or branched alkoxy, or 4-7 membered heterocycloalkyl containing 1-3 hetero atoms selected from the group consisting of N, O, and S; and

[188] R², R³ and R⁴ is independently -H, C₁₋₁₀ straight or branched alkyl, or C₁₋₁₀ straight or branched alkoxy.

[189]

[190] Preferably,

[191] R¹ is -H, C₁₋₅ straight or branched alkyl, C₁₋₅ straight or branched alkoxy, or 4-6 membered heterocycloalkyl containing 2-3 hetero atoms selected from the group consisting of N, O, and S.

[192]

[193] More preferably,

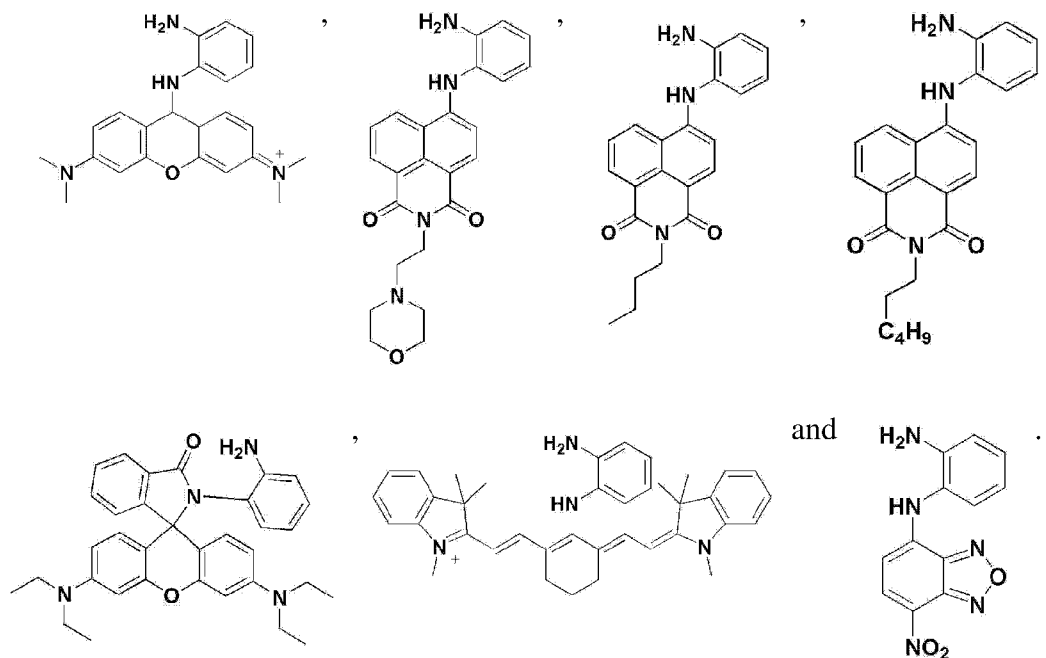
[194] R¹ is C₁₋₄ straight or branched alkyl, or 6 membered heterocycloalkyl containing 2-3 hetero atoms selected from the group consisting of N, O, and S.

[195]

[196] Most preferably,

[197] the compound represented by formula 1 above is the compound selected from the group consisting of the following compounds.

[198]



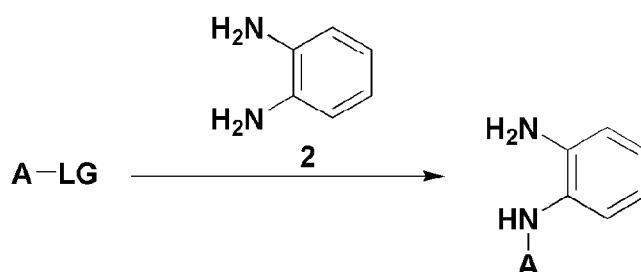
[199]

[200] The present invention also provides a method for preparing the compound represented by formula 1 containing the step of reacting the compound represented by A-LG with the compound represented by formula 2 to give the compound represented by formula 1 (step 1) as shown in the below reaction formula 1.

[201] [Reaction Formula 1]

[202]

STEP 1



[203] In the reaction formula 1, A is as defined in formula 1 of claim 1; and

[204] LG is =O, =S or halogene.

[205]

[206] Hereinafter, the method for preparing the compound represented by formula 1 of the present invention is described in more detail step by step.

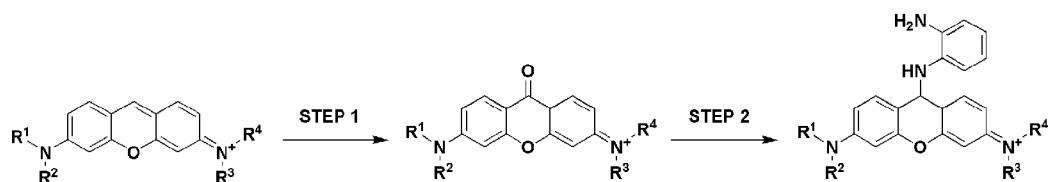
[207] In the method for preparing the compound represented by formula 1 of the invention, step 1 is to give the compound represented by formula 1 by reacting the compound represented by A-LG with the compound represented by formula 2.

[208] At this time, the compound represented by formula 1 is prepared by the method

shown in reaction formula 2, reaction formula 3, reaction formula 4, reaction formula 5, or reaction formula 6.

[209] [Reaction Formula 2]

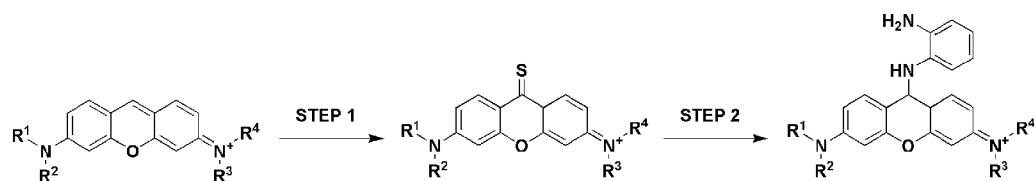
[210]



[211]

[212] [Reaction Formula 3]

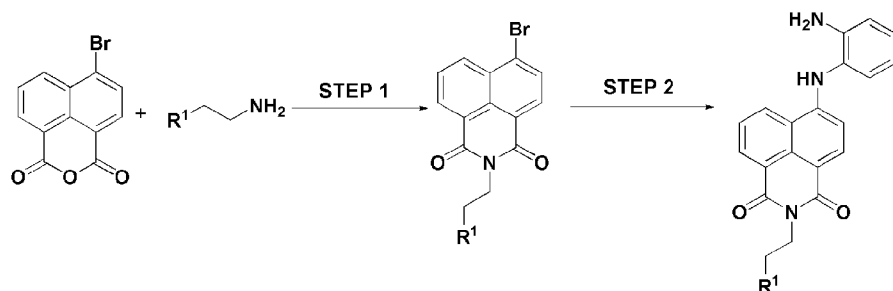
[213]



[214]

[215] [Reaction Formula 4]

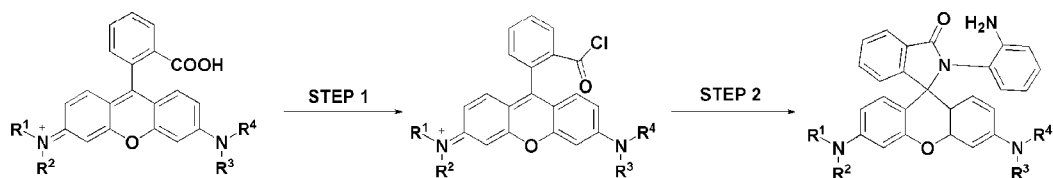
[216]



[217]

[218] [Reaction Formula 5]

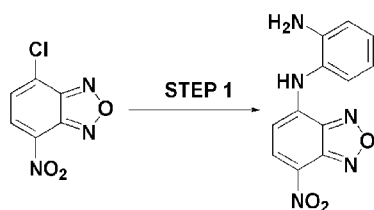
[219]



[220]

[221] [Reaction Formula 6]

[222]



[223]

[224] Further, the present invention provides a composition for detecting phosgene or DCP (diethyl chlorophosphate) comprising the compound represented by formula 1.

[225] The present invention also provides a kit for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) comprising the compound represented by formula 1.

[226] Herein, the detection is preferably performed by observing the changes of fluorescence or absorbance caused by the changes of π -conjugation system resulted from the nucleophilic attack of phenylenediamine included in the compound of claim 1 against phosgene or DCP (diethyl chlorophosphate).

[227]

[228] The present invention also provides a method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) comprising the following steps:

[229] contacting the detection kit of the invention with the sample to be analyzed (step 1); and

[230] evaluating the changes of fluorescence or absorption properties of the compound represented by formula 1 included in the detection kit after the contact of step 1 (step 2).

[231]

[232] Hereinafter, the method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) of the present invention is described in more detail step by step.

[233] In the method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) of the present invention, step 1 is to contact the detection kit with the sample to be analyzed.

[234] At this time, the sample herein is in the solid, liquid, or gas-phase, and more preferably in the liquid or gas-phase.

[235] The sample herein may include or not include phosgene or DCP (diethyl chlorophosphate), which is the detection target of this invention.

[236]

[237] In the method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) of the present invention, step 2 is to evaluate the changes of fluorescence or absorption properties of the compound represented by formula 1 included in the detection kit after the contact of step 1.

[238] Herein, when the sample contains phosgene or DCP (diethyl chlorophosphate), the detection target, the changes of fluorescence or absorption properties of the compound represented by formula 1 included in the detection kit can be observed.

[239]

[240] Another experiment was also performed to investigate whether or not the fluorescence or absorption properties were changed when the compound of example 1 of the invention was contacted with liquid-phase phosgene or DCP (diethyl chlorophosphate).

[241] As a result, it was confirmed that when the compound of example 1 of the invention was contacted with phosgene or DCP (diethyl chlorophosphate), the fluorescence or absorption properties were significantly changed so that they could be observed even with the naked eye (see Figures 1 and 2 of Experimental Examples 1 and 2).

[242] Another experiment was also performed to investigate whether or not the fluorescence or absorption properties were changed when the compound of example 1 of the invention was contacted with gas-phase phosgene or DCP (diethyl chlorophosphate).

[243] As a result, it was confirmed that when the compound of example 1 of the invention was contacted with phosgene or DCP (diethyl chlorophosphate), the fluorescence or absorption properties were significantly changed so that they could be observed even with the naked eye (see Figure 3 of Experimental Example 3).

[244] Further, an experiment was performed to evaluate whether or not the compound of example 2 of the invention was effective in detecting gas-phase phosgene. As a result, it was confirmed that the compound of example 2 was significantly effective in detecting gas-phase phosgene even with the naked eye (see Figures 4 ~ 11 of Experimental Examples 4 and 5).

[245] In addition, an experiment was performed to evaluate whether or not the compound of example 2 of the invention was effective in detecting liquid-phase phosgene. As a result, it was confirmed that the compound of example 2 was significantly effective in detecting liquid-phase phosgene by observing the changes of fluorescence properties (see Figure 12 of Experimental Example 6).

[246]

[247] Therefore, the compound of the present invention forms a different bond with phosgene or DCP to cause a change in the pi-conjugated system of the binding molecule, and the fluorescence and the color change according to the phosgene or DCP are different from each other. The compound has the effect of selectively detecting phosgene or DCP, respectively, or by mixing them.

[248]

[249] Practical and presently preferred embodiments of the present invention are illustrative as shown in the following Examples.

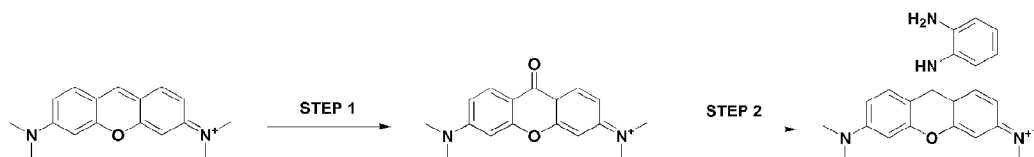
[250] However, it will be appreciated that those skilled in the art, on consideration of this disclosure, may make modifications and improvements within the spirit and scope of

the present invention.

[251]

[252] <Preparative Example 1> Preparation of o-phenylenediamine-pyronine(N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium)

[253]



[254] Step 1: Preparation of N-

(6-(dimethylamino)-9-oxo-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[255] N-(6-(dimethylamino)-3H-xandene-3-ylidene)-N-methylmethanaminium was reacted with KCN for 18 hours, reacted with FeCl₃/HCl for 12 hours, and then reacted with NaHCO₃, resulting in the preparation of N-(6-(dimethylamino)-9-oxo-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium.

[256]

[257] Step 2: Preparation of N-

(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[258] The compound prepared in step 1 above was reacted with Tf₂O and then reacted with benzene-1,2-diamine to give N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium (yield: 40%).

[259]

[260] <Example 1> Preparation of Compounds for Detecting Phosgene and DCP 1

[261] Step 1: Preparation of N-

(6-(dimethylamino)-9-thioxo-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[262]



[263] THF (40 ml) containing t-BuOK (0.56 g, 3 eq) was added to the solution containing Pyronine Y (N-(6-(dimethylamino)-3H-xandene-3-ylidene)-N-methylmethanaminium) (0.5 g, 1.65 m mol) and sulfur (0.79 g, 15 eq). The reaction mixture was refluxed for 10 hours. Termination of the reaction was confirmed by TLC. Then, the reaction mixture was cooled down at room temperature and filtered. Silica gel column chro-

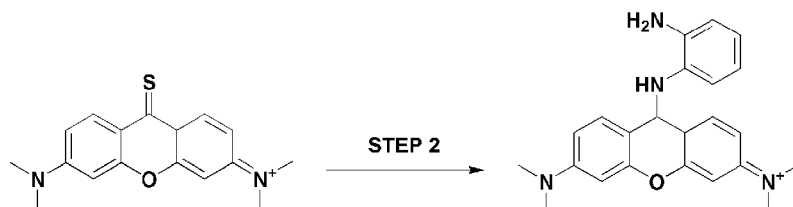
matography was performed with the residue (eluent, PE:DCM, 1:1) to give the target compound as a yellow solid (yield: 50%).

[264] ^1H NMR (300 MHz, CDCl_3), δ : 8.70 (d, $J = 9.2$ Hz, 2H), 6.75 (dd, $J = 9.2, 2.3$ Hz, 2H), 6.43 (d, $J = 2.3$ Hz, 2H), 3.13 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3), δ : 196.26, 154.58, 153.03, 131.80, 120.07, 110.52, 96.06, 40.24. ESI-MS: Calcd. for 299.11; Found 299.20.

[265]

[266] Step 2: Preparation of N-(9-(2-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[267]



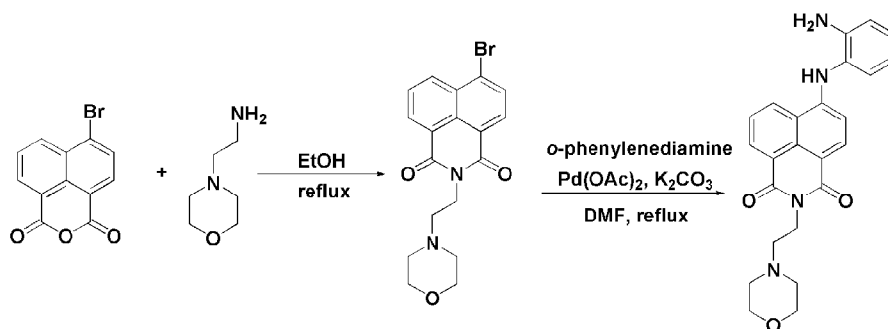
[268] 90 μl (2 eq) of Tf_2O was added drop by drop to the anhydrous CH_2Cl_2 solution (10 ml) containing 80 mg (0.268 mmol) of the compound prepared in step 1 above dissolved therein. The reaction mixture was well mixed with stirring at room temperature for 10 minutes. 0.29 g (10 eq) of o-phenylenediamine solution was added to the reaction mixture above, followed by stirring for 10 more hours. Then, CH_2Cl_2 was eliminated under reduced pressure. The solid residue was purified by silica gel chromatography (eluent, EA:DCM, 1:2) to give the target compound as a yellow solid (yield: 80%).

[269] ^1H NMR (300 MHz, MeOD), δ : 7.78 (d, $J = 9.5$ Hz, 2H), 7.25 (m, 1H), 7.09 (dd, $J = 7.8, 1.4$ Hz, 1H), 6.96 (dd, $J = 7.8, 1.4$ Hz, 1H), 6.81 (dd, $J = 3.9, 1.9$ Hz, 1H), 6.76 (m, 2H), 6.71 (d, $J = 2.5$ Hz, 2H), 3.18 (s, 12H). ^{13}C NMR (75 MHz, MeOD), δ : 157.01, 155.46, 154.03, 147.21, 143.91, 129.31, 126.98, 126.52, 117.72, 116.26, 110.67, 102.83, 96.68, 38.80. ESI-MS: $[\text{M}]^+$ Calcd. for 372.20; Found 372.30.

[270]

[271] <Example 2> Preparation of Compounds for Detecting Phosgene and DCP 2

[272]



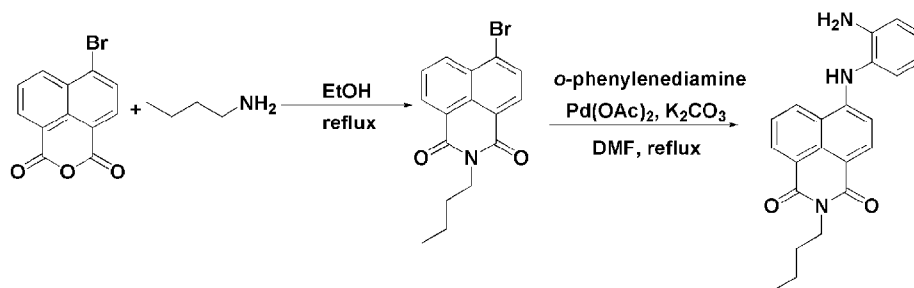
[273] To a solution of 4-bromo-1,8-naphthalene anhydride (1.38 g, 5.0 mmol) in anhydrous EtOH (20.0 ml) at room temperature was added 4-(2-aminoethyl)morpholine (715 mg, 5.5 mmol). After refluxing for 4 h, the reaction mixture was cooled and filtered to give 4-bromine-1,8-naphthalimide. This naphthalimide (389 mg, 1.0 mmol) and *o*-phenylenediamine (540 mg, 5.0 mmol) were dissolved in anhydrous DMF (20 mL). Subsequently, K₂CO₃ (550 mg, 4 mmol) and Pd(OAc)₂ (44 mg, 2 mmol) was added under nitrogen. The reaction was then refluxed overnight. The solvent DMF was then removed under vacuum. The crude product was treated with water, extracted with dichloromethane and dried over anhydrous MgSO₄. The organic layer was removed and the residue was purified by column chromatography to give 0.18 g of product (yellow solid, 43%).

[274] ¹H NMR (CDCl₃, 300MHz) δ (ppm) = 8.59 (m, 1H), 8.35 (d, 1H), 8.28 (d, 1H), 7.69 (m, 1H), 7.17 (m, 2H), 6.92-6.77 (m, 2H), 6.67 (d, 1H), 6.53 (s, 1H), 4.37-4.23 (m, 2H), 3.79 (s, 2H), 3.71-3.88 (m, 4H), 2.72-2.61, 2H), 2.57 (s, 4H). ¹³C NMR (75 MHz, CDCl₃) δ = 164.51, 163.89, 147.49, 142.82, 133.96, 131.31, 128.32, 127.44, 126.22, 125.32, 124.50, 123.21, 120.74, 119.50, 116.75, 112.30, 107.75, 67.02, 56.23, 53.80, 36.98. HRMS (ESI) *m/z* = 417.1718 [M + H]⁺, calcd for C₂₄H₂₅N₄O₃=417.1927.

[275]

[276] <Example 3> Preparation of Compounds for Detecting Phosgene and DCP 3

[277]



[278] To a solution of 4-bromo-1,8-naphthalene anhydride (1.38 g, 5.0 mmol) in anhydrous EtOH (20.0 ml) was added butylamine (480 mg, 5.5 mmol) at room temperature. After refluxing for 4 h, the reaction mixture was cooled and filtered to give 4-bromine-1,8-naphthalimide. This naphthalimide (540 mg, 5.0 mmol) and *o*-phenylenediamine (540 mg, 5.0 mmol) were dissolved in anhydrous DMF (20 mL). Subsequently, K₂CO₃ (550 mg, 4 mmol) and Pd(OAc)₂ (44 mg, 2 mmol) under nitrogen. The reaction was then refluxed overnight. The solvent DMF was then removed under vacuum. The crude product was treated with water, extracted with dichloromethane and dried over anhydrous MgSO₄. The organic layer was removed and the residue was purified by column chromatography to give 0.11 g of product (yellow solid, 61%).

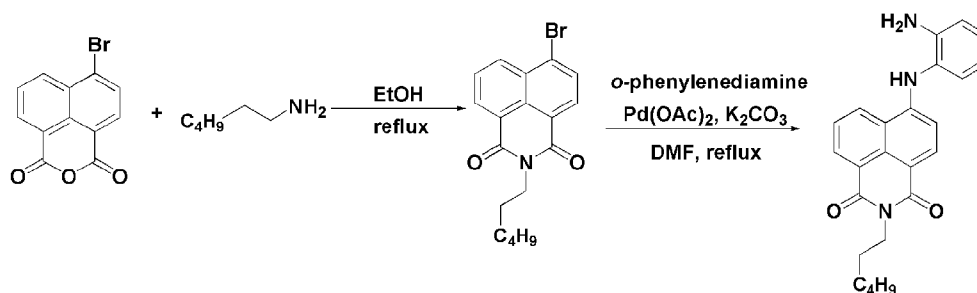
[279] ¹H NMR (DMSO-d₆, 300MHz) δ (ppm) = 9.01 (s, 1H), 8.91-8.88 (m, 1H), 8.50-8.47

(m, 1H), 8.20 (d, $J = 8.6\text{Hz}$, 1H), 7.78-7.73 (m, 1H), 7.09 (t, $J = 7.2\text{Hz}$, 2H), 6.88-6.84 (m, 1H), 6.69-6.63 (m, 1H), 6.41 (d, $J = 8.5\text{Hz}$, 1H), 5.04 (s, 2H), 4.16-3.89 (m, 2H), 1.58 (d, $J = 7.5\text{Hz}$, 2H), 1.47-1.19 (m, 2H), 0.92 (t, $J = 7.3\text{Hz}$, 3H); ^{13}C NMR DMSO- d_6 , $\delta = 164.47, 163.63, 150.48, 145.65, 134.54, 131.47, 130.23, 130.05, 128.82, 128.44, 125.14, 123.99, 122.55, 121.34, 117.19, 116.35, 109.79, 107.01, 55.61, 30.53, 20.51, 14.46$. HRMS (ESI) $m/z = 360.1706$ [$M + H$] $^+$, calcd for $\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_3 = 360.1712$.

[280]

[281] <Example 4> Preparation of Compounds for Detecting Phosgene and DCP 4

[282]

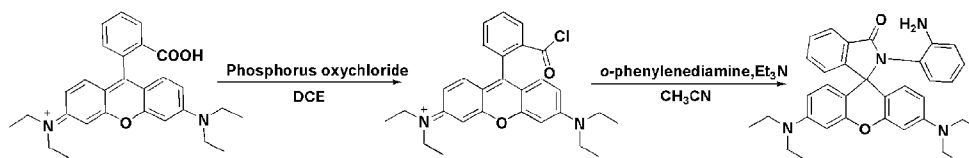


[283] The target compound was prepared by conducting the same synthesis as in Example 3 except that hexylamine was used instead of the butylamine used in Example 3.

[284]

[285] <Example 5> Preparation of Compounds for Detecting Phosgene and DCP 5

[286]



[287] To a solution of rhodamine B base (1.01 g, 2.3 mmol) in dry 1,2-dichloroethane (8.0 mL) at room temperature was added phosphorus oxychloride (6.9 mmol) over a period of 5 min. After being stirred at reflux for 4 h, the mixture was cooled and concentrated under vacuum to give the crude rhodamine B acid chloride. A solution of the acid chloride in dry acetonitrile (10 mL) was added dropwise to a solution of o-diaminobenzene (14 mmol) in dry acetonitrile (6.0 mL) containing triethylamine (8.0 mL). After being stirred for 4 h at room temperature, the mixture was concentrated under vacuum, and the residue was subjected to column chromatography to give target compound as a white solid in 83% yield.

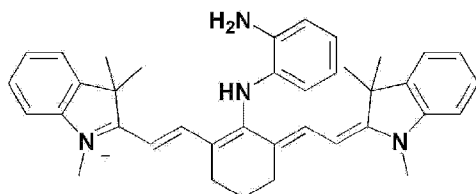
[288] ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 8.03-8.05 (m, 1H); 7.53-7.60 (m, 2H); 7.25-7.27 (m, 1H); 6.94 - 6.99 (m, 1H); 6.68 (d, $J = 8.7\text{Hz}$, 2H); 6.58 (dd, $J = 7.8\text{Hz}$, $J = 1.2\text{Hz}$, 1H); 6.40-6.46 (m, 1H); 6.31 (d, $J = 8.7\text{Hz}$, 2H); 6.28 (b, 2H); 6.10 (dd, $J = 8.1\text{Hz}$, $J = 1.5\text{Hz}$, 1H); 3.44 (s, 2H); 3.35 (q, $J = 6.9\text{Hz}$, 8H); 1.16 (t, $J = 7.2\text{Hz}$, 12H).

^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 166.63, 161.22, 154.20, 152.66, 149.15, 144.75, 132.81, 129.03, 128.97, 128.85, 128.55, 124.51, 123.66, 122.46, 118.43, 117.23, 108.21, 98.28, 68.27, 44.60, 31.15, 12.76. HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{36}\text{N}_4\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 533.2565. Found 533.2838.

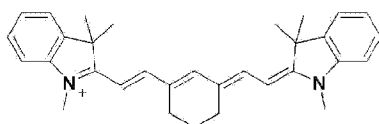
[289]

[290] <Example 6> Preparation of Compounds for Detecting Phosgene and DCP 6

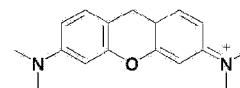
[291]



[292] The target compound was prepared by carrying out the same synthesis as in Example 1 except that



was used instead of

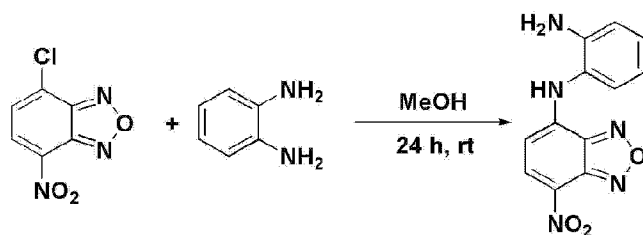


in the step 1 of Example 1 above.

[293]

[294] <Example 7> Preparation of Compounds for Detecting Phosgene and DCP 7

[295]



[296] To a solution of o-phenylenediamine (0.32 g, 3.0 mmol) in methanol (10 mL) was added NBD-Cl (0.20 g, 1.0 mmol) in methanol (10 mL) at room temperature with stirring. The resulting mixture was stirred at room temperature for 24 hours. Filtered and washed several times with methanol to give a target compound (reddish brown solid, 71%).

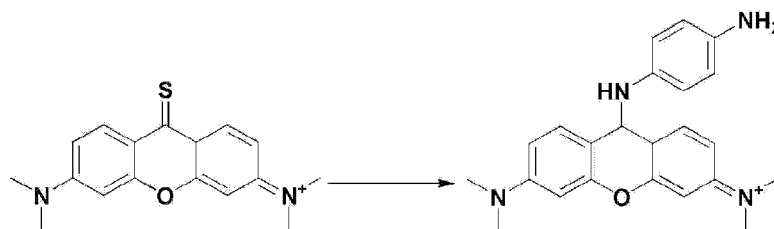
[297] ^1H NMR (DMSO-d_6 , 300 MHz) : δ 10.69 (brs, 1H), 8.54 (d, $J = 8.7$ Hz, 1H), 7.09-7.15 (m, 2H), 6.84 (d, $J = 7.2$ Hz, 1H), 6.64 (t, $J = 7.8$ Hz, 1H), 5.93 (d, $J = 8.7$ Hz, 1H), 5.27 (brs, 2H). ^{13}C NMR (DMSO-d_6 , 75MHz) : δ 145.49, 145.04, 144.96, 144.92, 138.58, 129.44, 128.14, 121.95, 116.77, 116.49, 113.59, 102.34. HRMS (EI) $m/z = 270.0640$ [M] $^+$, calcd for $\text{C}_{12}\text{H}_9\text{N}_5\text{O}_3 = 270.0704$.

[298]

[299] <Comparative Example 1> Preparation of N-(9-(4-aminophenylamino)-6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-meth

ylmethanaminium

[300]



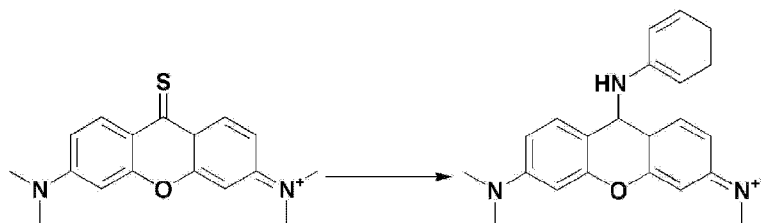
[301] 50 mg (0.168 m mol) of the compound prepared in step 1 of example 1 was dissolved in CH_2Cl_2 (10 ml), to which 57 μl (2 eq) of Tf_2O was added drop by drop. The reaction mixture was stirred for 10 minutes, to which 235 μl (15 eq) of phenylamine was added. The mixture was stirred at room temperature for overnight. Upon completion of the reaction, CH_2Cl_2 was eliminated under reduced pressure. The solid residue was purified by silica gel chromatography (eluent, EA:DCM, 1:3) to give the target compound as an orange solid (yield: 70%).

[302] ^1H NMR (300 MHz, MeOD), δ : 7.67 (d, J = 9.5 Hz, 2H), 7.56 (dd, J = 7.7, 6.6 Hz, 2H), 7.46 (m, 1H), 7.40 (d, J = 7.7 Hz, 2H), 6.80 (dd, J = 9.5, 2.4 Hz, 2H), 6.73 (d, J = 2.4 Hz, 2H), 3.19 (s, 12H). ^{13}C NMR (75 MHz, MeOD), δ : 157.34, 155.65, 153.33, 140.66, 129.94, 127.66, 127.16, 125.05, 110.83, 102.73, 96.32, 38.86. ESI-MS: $[\text{M}]^+$ Calcd for 358.19; Found 358.30.

[303]

[304] <Comparative Example 2> Preparation of N-(6-(dimethylamino)-9-(phenylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium

[305]



[306] 100 mg (0.336 m mol) of the compound prepared in step 1 of example 1 was dissolved in CH_2Cl_2 (15 ml), to which 114 μl (2 eq) of Tf_2O was added drop by drop. The reaction mixture was stirred for 10 minutes, to which 0.54 g (15 eq) of p-phenylenediamine was added. The mixture was stirred at room temperature for overnight. Upon completion of the reaction, the solvent was eliminated under reduced pressure. The solid residue was purified by silica gel chromatography (eluent, DCM:EtOH, 30:1) to give the target compound as a yellow solid (yield: 70%).

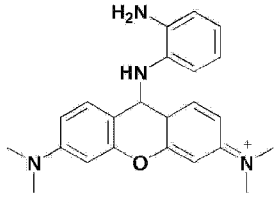
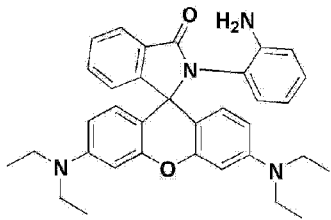
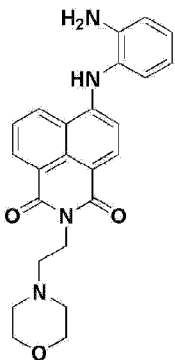
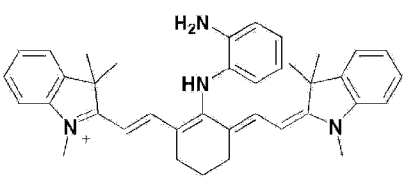
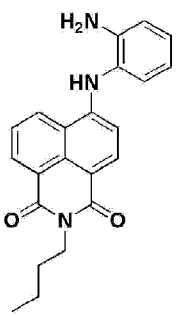
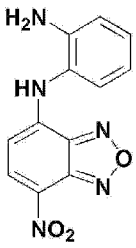
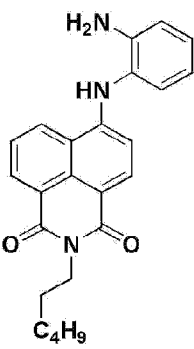
[307] ^1H NMR (300 MHz, MeOD) δ 7.74 (s, 2H), 7.13 (m, 2H), 6.84 (m, 4H), 6.70 (d, J = 2.5 Hz, 2H), 3.18 (s, 12H). ^{13}C NMR (75 MHz, MeOD) δ 157.01, 154.99, 150.34,

129.75, 128.51, 127.92, 116.80, 112.16, 103.60, 97.75, 40.26. [M]⁺ calcd for 373.20, Found 373.30.

[308]

[309] The chemical formulae of the compounds prepared in examples 1 ~ 7 are shown in Table 1.

[310] [Table 1]

Example	Chemical Formula	Example	Chemical Formula
1		5	
2		6	
3		7	
4			

[311]

[312] <Experimental Example 1> Evaluation of phosgene detection ability of the compound of example 1

[313] The following experiment was performed in order to evaluate the phosgene detection ability of the compound prepared in example 1.

[314] Particularly for the safety of the experiment, non-volatile and relatively less toxic triphosgene, the precursor of phosgene, was used instead of the volatile phosgene to evaluate the detection ability of the compound prepared in example 1. The compound of example 1 was loaded in chloroform at the concentration of 10 μ M, to which triphosgene was added with different concentrations (0-2 eq), during which the changes of fluorescence and absorbance were observed to evaluate the phosgene detection ability. The results are shown in Figure 1. In the experiment, excitation wavelength was 580 nm and slit width was 1.5 nm. Each spectrum was measured at 2 min intervals.

[315] Figure 1(a) is a graph illustrating the fluorescence spectrum of the compound of example 1 of the invention according to the concentration of phosgene, wherein the fluorescence photograph is on the right side of the graph. Figure 1(b) is a graph illustrating the absorption spectrum of the compound of example 1 of the invention according to the concentration of phosgene, wherein the color development photograph is on the right side of the graph.

[316] As shown in Figure 1(a), the fluorescence intensity of the compound of example 1 of the invention was stronger as the concentration of phosgene was increased, and thus red fluorescence was observed with the naked eye. As shown in Figure 1(b), wavelength band of the absorption spectrum of the compound of example 1 of the invention was changed as the concentration of phosgene was increased. The color thereof started yellow and turned purple, which was also observed with the naked eye.

[317] Therefore, the compound for detecting phosgene of the present invention can be effectively used as a composition for detecting phosgene since the changes of fluorescence and color development can be observed with the naked eye.

[318]

[319] <Experimental Example 2> Evaluation of DCP (diethyl chlorophosphate) detection ability of the compound of example 1

[320] The following experiment was performed by the same manner as described in experimental example 1 in order to evaluate the DCP detection ability of the compound prepared in example 1 of the invention except that DCP (diethyl chlorophosphate) was used instead of phosgene. The results are shown in Figure 2.

[321] Figure 2(a) is a graph illustrating the fluorescence spectrum of the compound of example 1 of the invention according to the concentration of DCP (diethyl chlorophosphate), wherein the fluorescence photograph is on the right side of the graph.

[322] Figure 2(b) is a graph illustrating the absorption spectrum of the compound of

example 1 of the invention according to the concentration of DCP (diethyl chlorophosphate).

[323] As shown in Figure 2(a), the fluorescence intensity of the compound of example 1 of the invention was stronger as the concentration of DCP (diethyl chlorophosphate) was increased, and thus green fluorescence was observed with the naked eye.

[324] As shown in Figure 2(b), wavelength band of the absorption spectrum of the compound of example 1 of the invention was changed as the concentration of DCP (diethyl chlorophosphate) was increased.

[325] Therefore, the compound for the detection of DCP (diethyl chlorophosphate) of the present invention can be effectively used as a composition for the detection of DCP (diethyl chlorophosphate) since the changes of fluorescence and color development can be observed with the naked eye.

[326]

[327] <Experimental Example 3> Evaluation of gas-phase phosgene and DCP (diethyl chlorophosphate) detection ability of the compound of example 1

[328] The following experiment was performed in order to evaluate the gas-phase phosgene and DCP detection ability of the compound of example 1 of the invention.

[329] Particularly, in order to evaluate whether or not the compound prepared in example 1 could act as a real sensor to detect gas-phase phosgene and DPC efficiently, a kit was constructed wherein the compound of example 1 was fixed on polyethylene oxide film. The kit was exposed on different concentrations of phosgene and DCP (0-20 ppm), followed by observation of the changes of fluorescence and color development in the compound of example 1. The results are shown in Figure 3.

[330] Figure 3(a) is an image illustrating the changes of fluorescence resulted from the exposure on gas-phase phosgene or gas-phase DCP (diethyl chlorophosphate). Precisely, the compound of example 1 was prepared as a sensor which was exposed on gas-phase phosgene or gas-phase DCP, followed by observation of the changes of fluorescence.

[331] Figure 3(b) is an image illustrating the changes of color development resulted from the exposure on gas-phase phosgene or gas-phase DCP (diethyl chlorophosphate). Precisely, the compound of example 1 was prepared as a sensor which was exposed on gas-phase phosgene or gas-phase DCP, followed by observation of the changes of color development.

[332] As shown in Figure 3, the compound of the example of the present invention can be useful as a sensor to detect the changes of fluorescence and color development according to the exposure on gas-phase phosgene and DCP (diethyl chlorophosphate).

[333]

[334] <Experimental Example 4> Evaluation 1 of phosgene detection ability of the

compound of example 2

- [335] The following experiment was performed to evaluate whether or not the compound of example 2 was useful for the detection of gas-phase phosgene.
- [336] A filter paper was cut into 2 cm x 1 cm and dipped in DCM solution (1 mg/mL) containing the compound of example 2 dissolved therein. The filter paper was dried to eliminate the solvent. Then, the filter paper was placed in a sealed flask containing 0.2 mg of phenanthridine and 0.2 mg of triphosgene. The concentration of phosgene therein was 0.8 mg/L (Figure 4) or 8 mg/L (Figure 5). The filter paper, exposed or not exposed on 0.8 mg/L or 8 mg/L of phosgene, was photographed at 365 nm (Figures 6 ~ 8).
- [337] Figure 4 is a photograph illustrating the experimental step to contact the filter-paper retaining the compound of example 2 with 0.8 mg/L of phosgene.
- [338] Figure 5 is a photograph illustrating the experimental step to contact the filter-paper retaining the compound of example 2 with 8 mg/L of phosgene.
- [339] Figure 6 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 without the exposure on phosgene, photographed at 365 nm.
- [340] Figure 7 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 and exposed on 0.8 mg/L of phosgene, photographed at 365 nm.
- [341] Figure 8 is a photograph illustrating the image of the filter-paper retaining the compound of example 2 and exposed on 8 mg/L of phosgene, photographed at 365 nm.
- [342] As shown in Figures 6 ~ 8, color of the filter-paper retaining the compound of example 2 exposed on phosgene was changed, compared with the filter-paper retaining the compound of example 2 not-exposed on phosgene.
- [343] Therefore, it was confirmed that gas-phase phosgene could be easily detected by using the compound of example 2 with the naked eye.

[344]

[345] <Experimental Example 5> Evaluation 2 of phosgene detection ability of the compound of example 2

- [346] The following experiment was performed to evaluate whether or not the compound of example 2 was useful for the detection of gas-phase phosgene.
- [347] The gas-phase phosgene detection ability of the compound of example 2 was evaluated by the same manner as described in example 4 except that a thin glass plate was used. The results are shown in Figures 9 ~ 11.
- [348] Figure 9 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 without the exposure on phosgene.
- [349] Figure 10 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 which was exposed on 0.8 mg/L of phosgene.

- [350] Figure 11 is a photograph illustrating the luminescence of the glass plate coated with the compound of example 2 which was exposed on 8 mg/L of phosgene.
- [351] As shown in Figures 9 ~ 11, fluorescence properties of the glass plate coated with the compound of example 2 exposed on phosgene were changed, compared with the glass plate coated with the compound of example 2 not-exposed on phosgene.
- [352] Therefore, it was confirmed that the compound of example 2 of the invention is effective in detecting gas-phase phosgene by observing the changes of fluorescence properties.
- [353]
- [354] <Experimental Example 6> Evaluation 3 of phosgene detection ability of the compound of example 2
- [355] The following experiment was performed to evaluate whether or not the compound of example 2 was useful for the detection of liquid-phase phosgene.
- [356] 30 µg of the compound of example was absorbed in 30 mg of silica gel, which was treated with 3 µg or 30 µg of triphosgene dissolved in chloroform. Then, the changes of fluorescence properties were observed and one of the results is presented in Figure 12.
- [357] Figure 12 is a photograph illustrating the fluorescence characteristics of the silica gel retaining the compound of example 2 after the treatment of 30 µg triphosgene.
- [358] As shown in Figure 12, fluorescence properties of the silica gel retaining the compound of example 2 treated with phosgene were changed, compared with the silica gel retaining the compound of example 2 not-treated with phosgene.
- [359] Therefore, it was confirmed that the compound of example 2 of the invention is effective in detecting liquid-phase phosgene by observing the changes of fluorescence properties.
- [360]
- [361] In the above Experimental Examples 1-7, it was found that the compounds according to the present invention react with phosgene or DCP in a gaseous or liquid state to induce changes in fluorescence and color development at nM concentration, which induces different changes according to whether it is a phosgene or a DCP. Accordingly, the compounds of the invention or compositions containing the same may be usefully employed for phosgene and DCP detection, And can be used in the entire industry as a detection composition and a kit which are capable of selectively detecting and sensitively detecting to exposure of phosgene and DCP.

[362]

Industrial Applicability

- [363] The compound for detecting phosgene and DCP (diethyl chlorophosphate) of the

present invention can selectively detect phosgene and DCP (diethyl chlorophosphate) either in the liquid phase or gas phase by detecting the changes of fluorescence and color development very quickly within a few seconds with nM sensitivity. Therefore, the compound can be effectively used as a composition and a kit for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate). In particular, it can be useful in the field where human resources must be protected from the exposure of phosgene and DCP (diethyl chlorophosphate).

[364]

[365] Those skilled in the art will appreciate that the conceptions and specific embodiments disclosed in the foregoing description may be readily utilized as a basis for modifying or designing other embodiments for carrying out the same purposes of the present invention. Those skilled in the art will also appreciate that such equivalent embodiments do not depart from the spirit and scope of the invention as set forth in the appended claims.

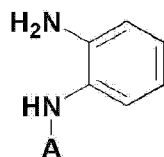
[366]

Claims

[Claim 1]

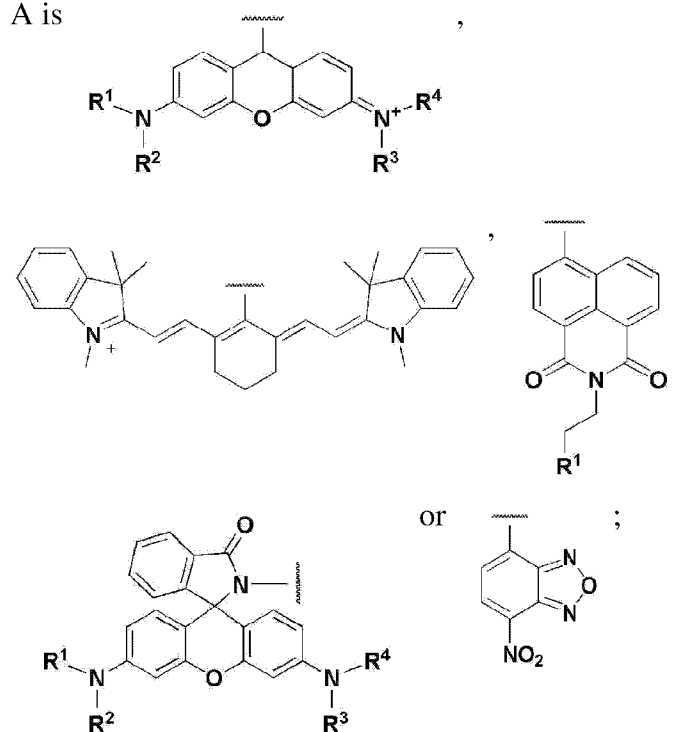
A compound represented by formula 1 below:

[Formula 1]



(In the formula 1,

A is



The above R¹ is -H, C₁₋₁₀ straight or branched alkyl, C₁₋₁₀ straight or branched alkoxy, or 4-7 membered heterocycloalkyl containing 1-3 hetero atoms selected from the group consisting of N, O, and S; and The above R², R³ and R⁴ is independently -H, C₁₋₁₀ straight or branched alkyl, or C₁₋₁₀ straight or branched alkoxy).

[Claim 2]

The compound according to claim 1, wherein R¹ is -H, C₁₋₅ straight or branched alkyl, C₁₋₅ straight or branched alkoxy, or 4-6 membered heterocycloalkyl containing 2-3 hetero atoms selected from the group consisting of N, O, and S.

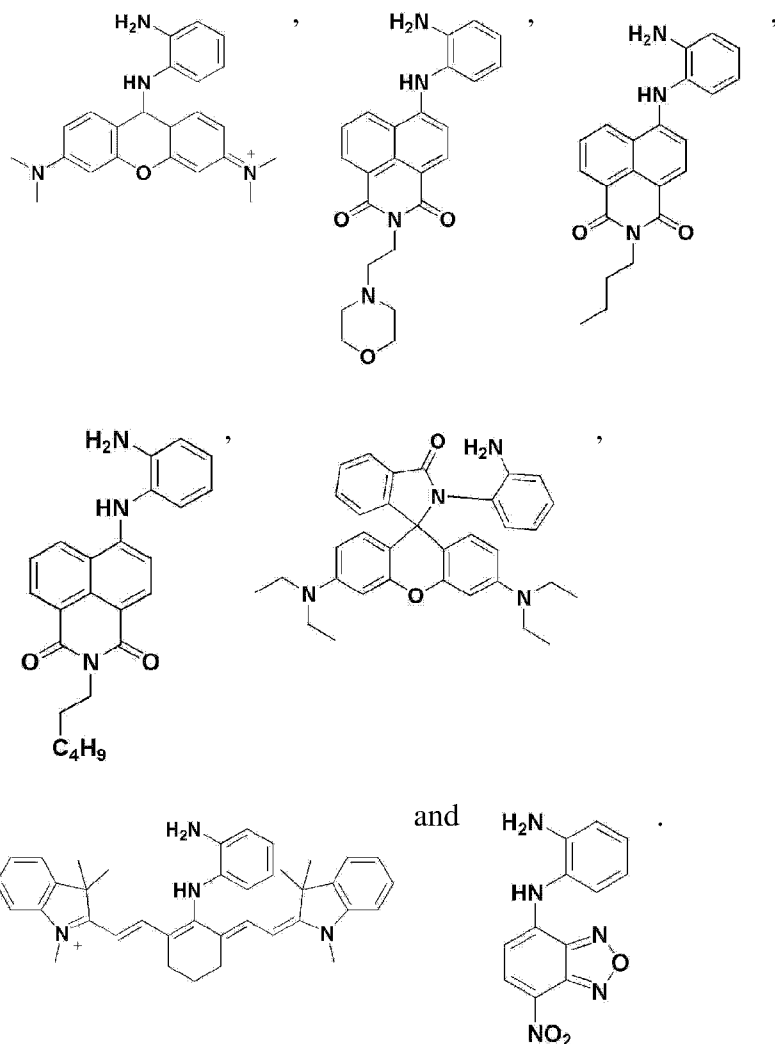
[Claim 3]

The compound according to claim 1, wherein R¹ is C₁₋₄ straight or branched alkyl, or 6 membered heterocycloalkyl containing 2-3 hetero atoms selected from the group consisting of N, O, and S.

[Claim 4]

The compound according to claim 1, wherein the compound rep-

represented by formula 1 above is the compound selected from the group consisting of the following compounds:

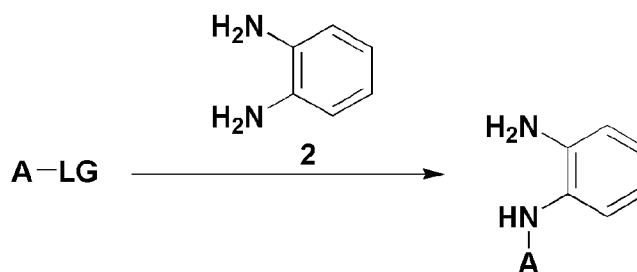


[Claim 5]

A method for preparing the compound represented by formula 1 of claim 1 containing the step of reacting the compound represented by A-LG with the compound represented by formula 2 to give the compound represented by formula 1 (step 1) as shown in the below reaction formula 1:

[Reaction Formula 1]

STEP 1



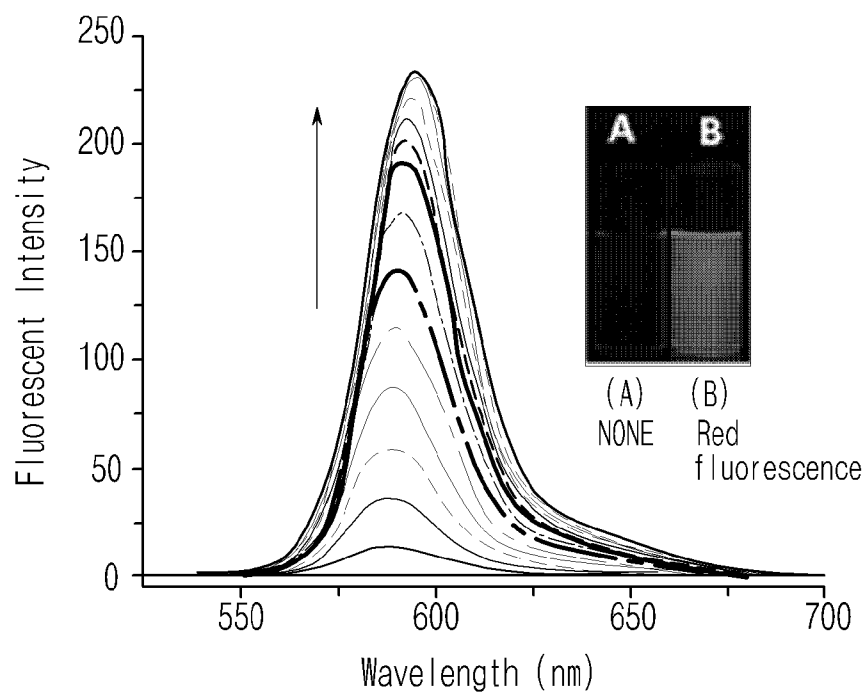
(In the reaction formula 1,

A is as defined in formula 1 of claim 1; and

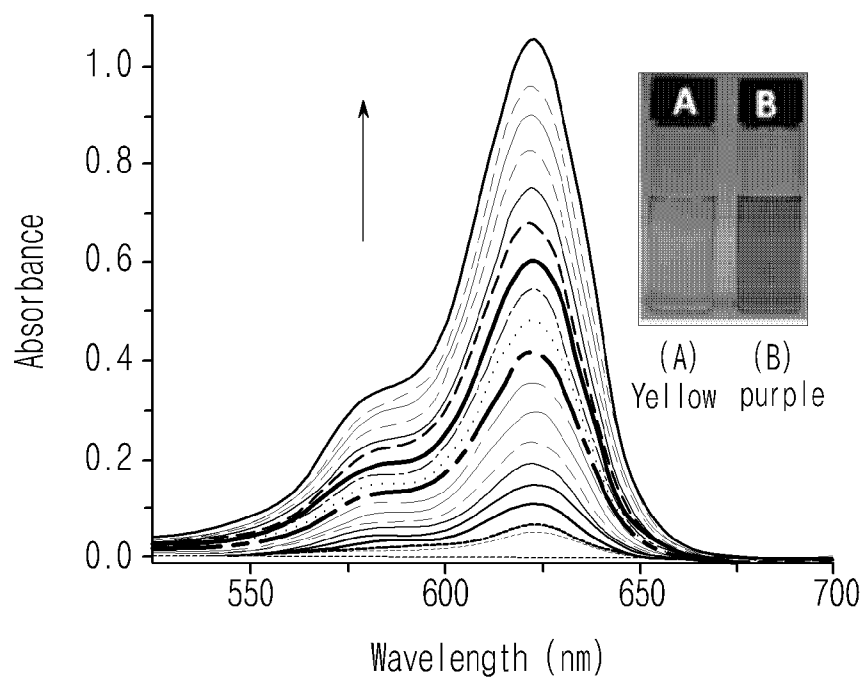
LG is =O, =S or halogene).

- [Claim 6] A composition for detecting phosgene comprising the compound of claim 1.
- [Claim 7] A composition for the detection DCP (diethyl chlorophosphate) comprising the compound of claim 1.
- [Claim 8] A kit for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) comprising the compound of claim 1.
- [Claim 9] The kit according to claim 8, wherein the kit is to detect the changes of fluorescence or absorbance caused by the changes of π -conjugation system of the compound of claim 1, which is resulted from the nucleophilic attack of phenylenediamine included in the compound of claim 1 against phosgene or DCP (diethyl chlorophosphate).
- [Claim 10] A method for the detection of one or more compounds selected from the group consisting of phosgene and DCP (diethyl chlorophosphate) comprising the following steps:
 contacting the kit of claim 8 with the sample to be analyzed (step 1);
 and
 evaluating the changes of fluorescence or absorption properties of the kit of claim 8 after the contact of step 1 (step 2).

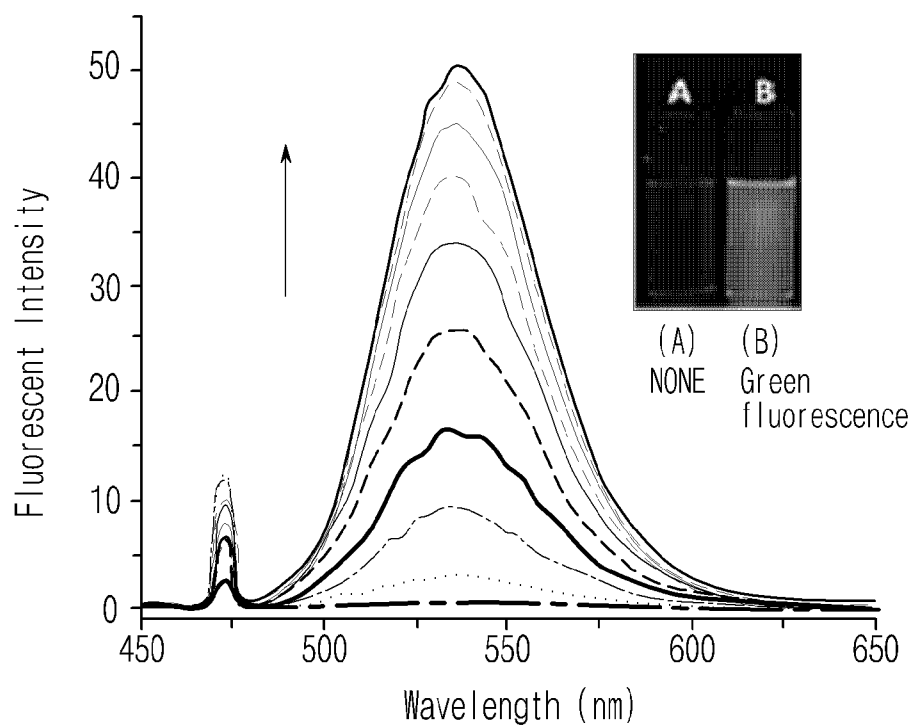
[Fig. 1a]



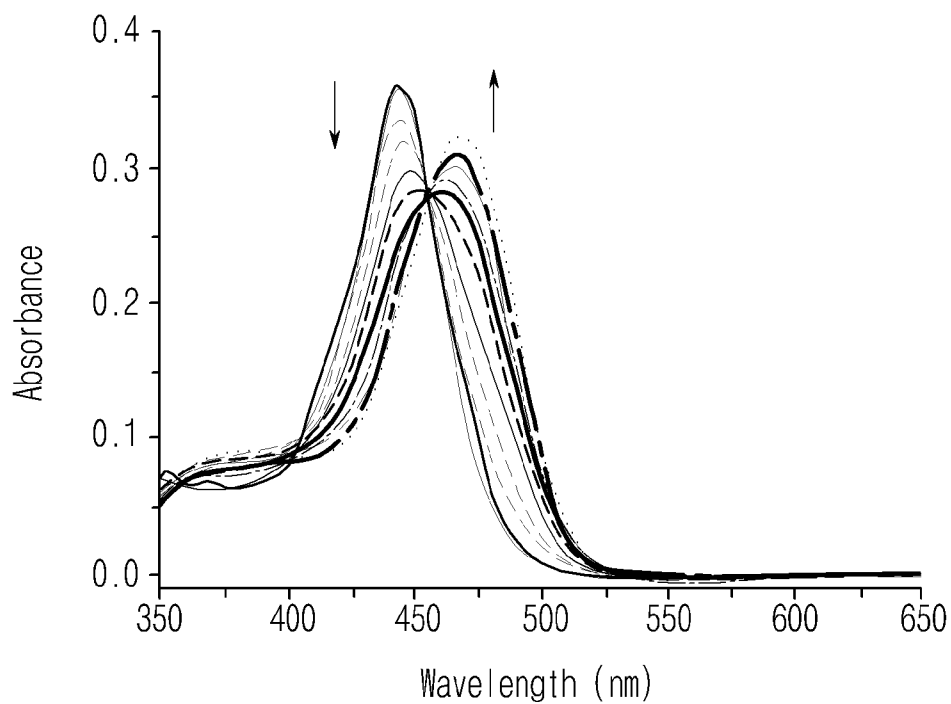
[Fig. 1b]



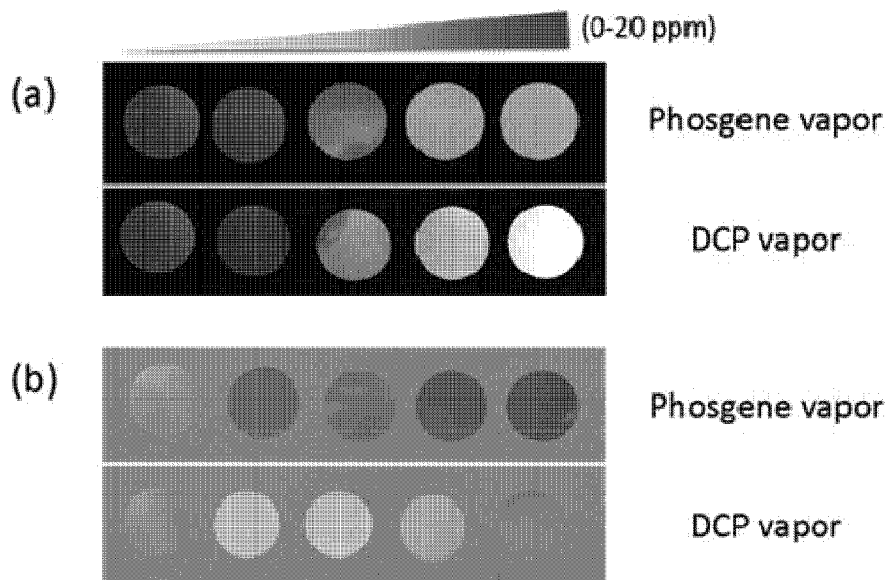
[Fig. 2a]



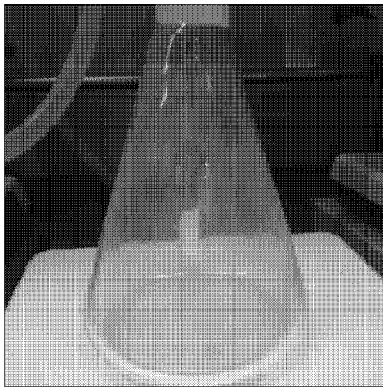
[Fig. 2b]



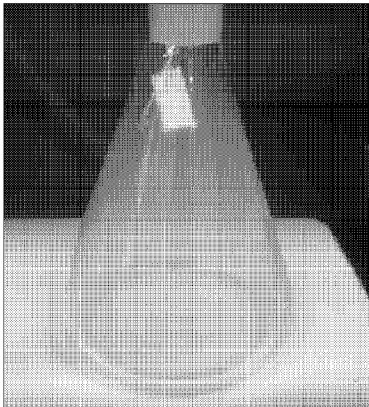
[Fig. 3]



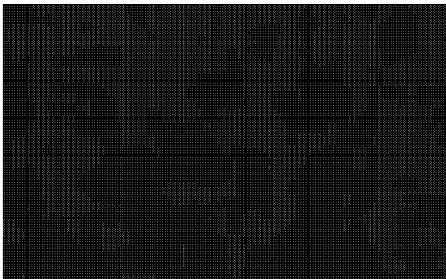
[Fig. 4]



[Fig. 5]

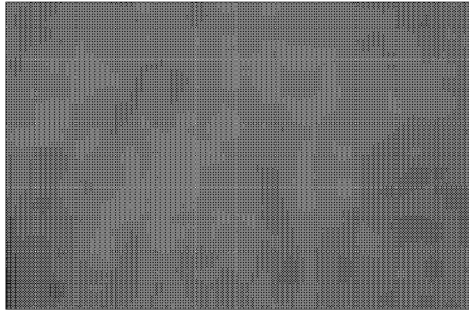


[Fig. 6]



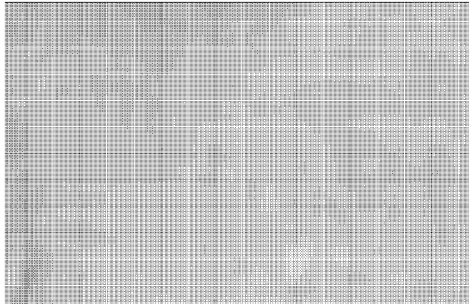
no phosgene exposure
no fluorescence, black

[Fig. 7]



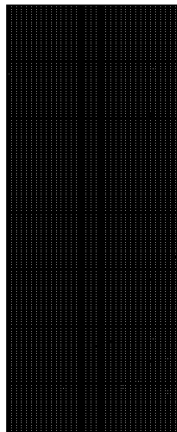
exposed on 0.8 mg/L of phosgene
fluorescence, green

[Fig. 8]



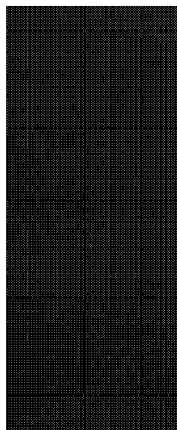
exposed on 8 mg/L of phosgene
fluorescence, cyan
(Stronger fluorescence than Figure 7)

[Fig. 9]



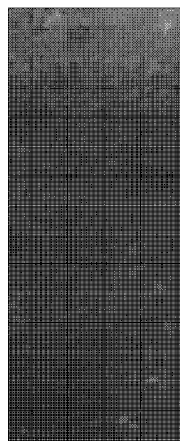
no phosgene exposure
no fluorescence, black

[Fig. 10]



exposed on 0.8 mg/L of phosgene
fluorescence, dark blue

[Fig. 11]



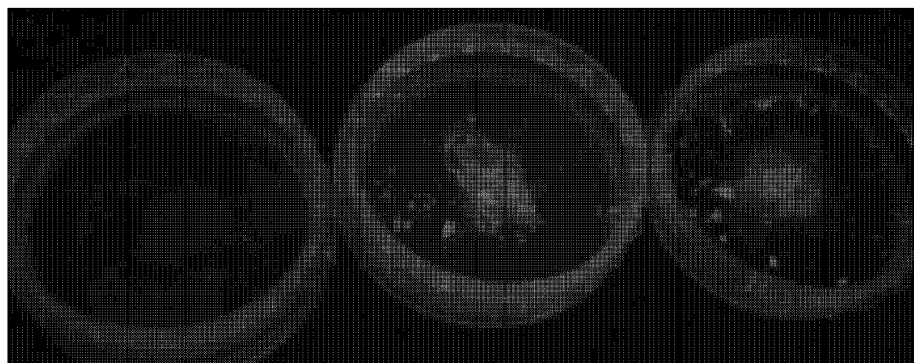
exposed on 8 mg/L of phosgene
fluorescence, blue
(Stronger fluorescence than Figure 10)

[Fig. 12]

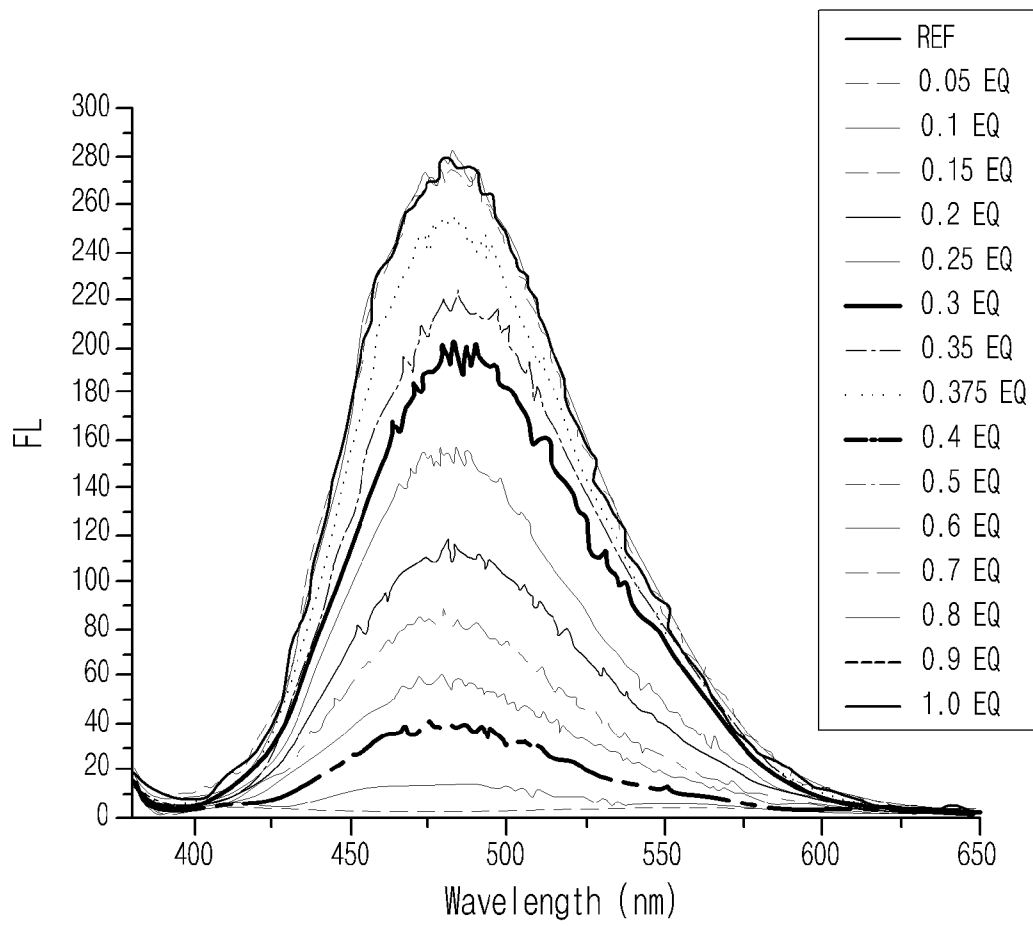
A

B

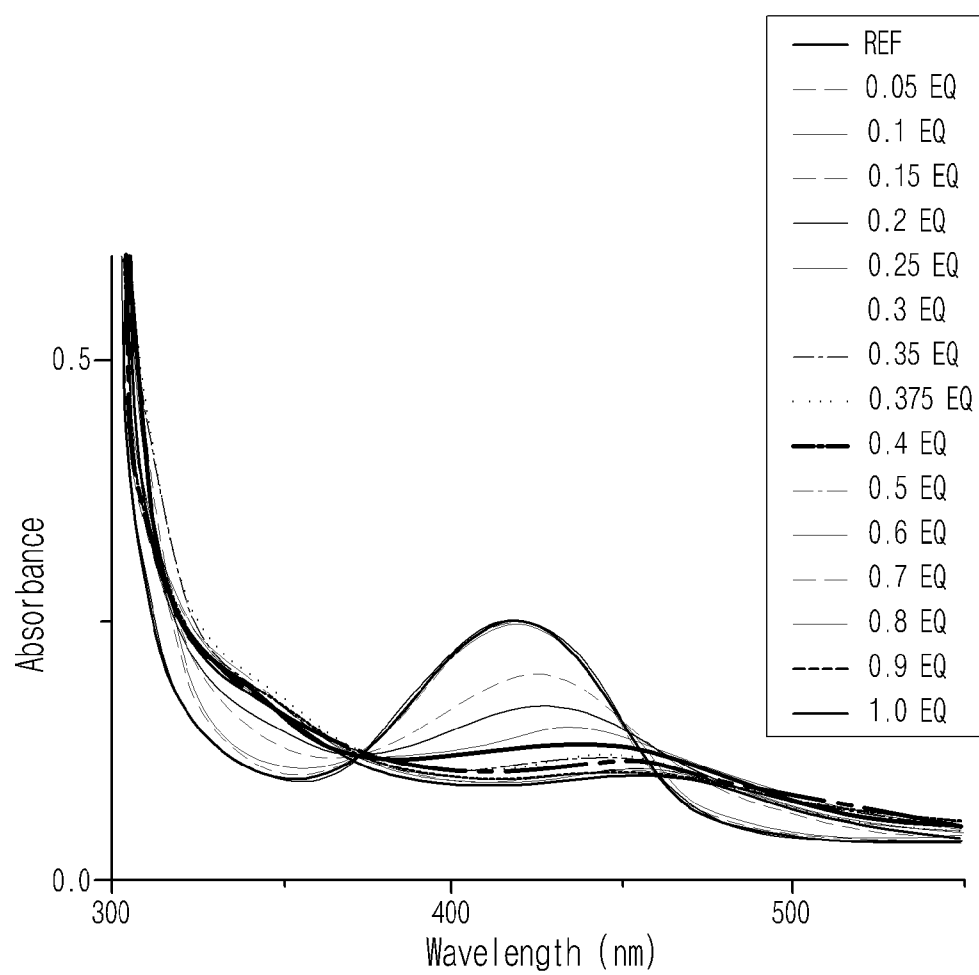
C



[Fig. 13a]



[Fig. 13b]



A. CLASSIFICATION OF SUBJECT MATTER

C07D 311/82(2006.01)i, C07D 221/14(2006.01)i, C07D 271/12(2006.01)i, C07D 209/08(2006.01)i, G01N 33/00(2006.01)i, G01N 21/64(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D 311/82; C07D 221/14; C07D 271/12; C07D 209/08; G01N 33/00; G01N 21/64

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal), STN (Registry, Caplus), Google & Keywords: 6-(dimethylamino)-9,9a-dihydroxandene-3-ylidene)-N-methylmethanaminium, ethyl-morpholine-naphthalene, phosgene, DCP(diethyl chlorophosphate), detect

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUN, Y.-Q. et al., "A mitochondria-targetable fluorescent probe for dual-channel NO imaging assisted by intracellular cysteine and glutathione", Journal of the American Chemical Society, 2014, Vol. 136, pages 12520-12523 See pages 12520, 12521; and schemes 1, 2.	1-10
X	KUMAR, V. et al., "A reaction based turn-on type fluorogenic and chromogenic probe for the detection of trace amount of nitrite in water", Talanta, 2012, Vol. 99, pages 610-615 See pages 611-613; and scheme 2.	1-10
X	LIN, C.-Y. et al., "A new selective colorimetric and fluorescent chemodosimeter for HSO ₄ ⁻ based on hydrolysis of Schiff base", Molecular and Biomolecular Spectroscopy, 2013, Vol. 115, pages 552-558 See pages 552, 553; and scheme 1.	1,4-10
A	WANG, X. et al., "Screening and investigation of a cyanine fluorescent probe for simultaneous sensing of glutathione and cysteine under single excitation", Chemical Communications, 2014, Vol. 50, pages 15439-15442 See page 15439; and figure 1.	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search

19 May 2017 (19.05.2017)

Date of mailing of the international search report

19 May 2017 (19.05.2017)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2017/001389

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	GUPTA, N. et al., "An approach for the selective detection of nitric oxide in biological systems: An in vitro and in vivo perspective", Chemistry - An Asian Journal, 5 April 2016, Vol. 11, No. 7, pages 1020-1027 See pages 1020, 1021; and scheme 2.	1-10
PX	ZHOU, X. et al., "A fluorescent sensor for dual-channel discrimination between phosgene and a nerve-gas mimic", Angewandte Chemie International Edition, [first published] 3 March 2016, Vol. 55, pages 4729-4733 See pages 4730, 4731; and schemes 2, 3.	1-10
PX	CHEN, L. et al., "A fluorescent sensor for dual channel discrimination between phosgene and a nerve gas mimic", In: The International Symposium on Macrocyclic and Supramolecular Chemistry, 10 July 2016 See abstract.	1-10
PX	YOON, J., "Fluorescent probes for hypochlorous acid and phosgene", In: 5th International Conference on Molecular Sensors and Molecular Logic Gates in the Chancellor's Building at the University of Bath, 24 July 2016 See abstract.	1-10
PX	HU, Y. et al., "Effective strategy for colorimetric and fluorescence sensing of phosgene based on small organic dyes and nanofiber platforms", ACS Applied Materials & Interfaces, 8 August 2016, Vol. 8, No. 34, pages 22246-22252 See abstract; pages 22247-22250; and figure 1.	1-10
PX	HU, Y. et al., "Small organic dyes and nanofiber platforms based effective strategy for colorimetric and fluorescence sensing of phosgene", In: The 118th General Meeting of the Korean Chemical Society, Korea busan, BEXCO, 12 October 2016 See abstract.	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

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