Supporting Information

Discriminating Detection between Mg^{2+} and Ca^{2+} by Fluorescent Signal from Anthracene aromatic amide moiety

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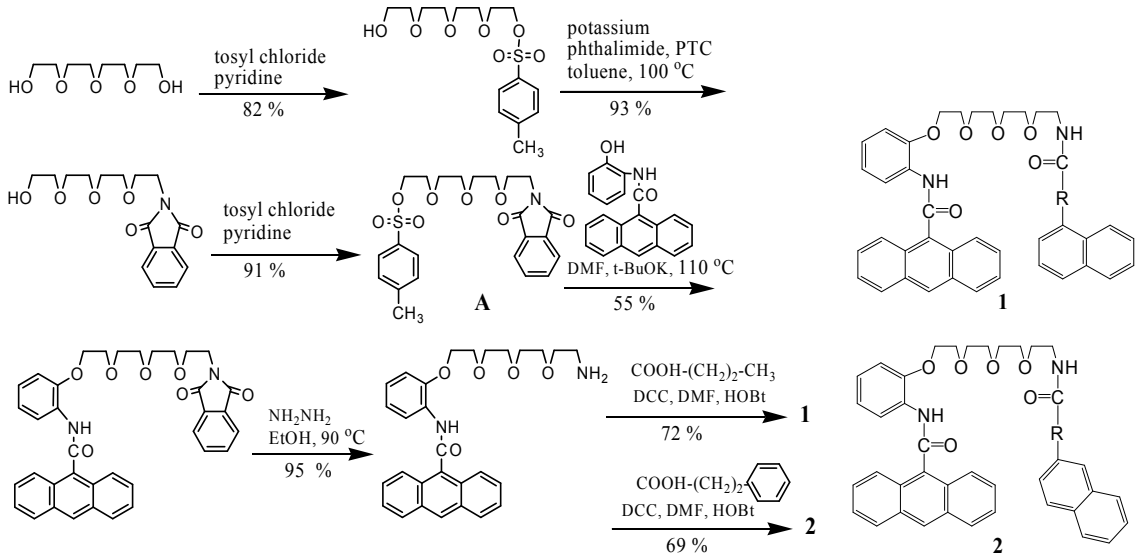
Experimental Details for syntheses of compounds 1 and 2

Tetraethylene glycol (3.88 g, 0.02 mol) in pyridine (50 mL) was stirred under 10 ºC for 1h with the addition of *p*-toluenesulfonly chloride (3.80 g, 0.02 mol), and was stored in refrigerator for 1 day. The solution was treated with HCl and water, and extracted by benzene, and then $CHCl_3$. The $CHCl_3$ phase was dried with $MgSO_4$, and evaporated. The residue was dissolved in toluene (80 mL), and refluxed with addition of potassium phthalimide (3.01g, 0.016 mol) and tri-butylhexadecyl phosphonium bromide (1.1 g, 0.0002 mol). The reaction mixture was filtered, and evaporated. The residue was tosylated as above, once more. The crude product (compound **A**) was purified by chromatography on silica gel column with chloroform / hexane (9:1) as eluent. Compound **A** (3.29 g, 0.014 mol) in 20 mL of DMF was added dropwise to DMF solution (20mL) of *t*-BuOK (1.12 g, 0.0014 mol) and *N*-(2-hydroxyphenyl)-9-anthryl-amide (3.14 g, 0.0014 mol). The reaction mixture was heated for 1 day at 110 °C. The reaction mixture was evaporated under reduced pressure, and was dissolved in $CHCl_3$. The solution was washed with distilled water, dried over $MgSO_4$, and evaporated. The residue was dissolved in 80mL of EtOH, and treated with $NH_2NH_2{\cdot}H_2O$ (1.7 g, 0.03 mol) under reflux for 4 h at 90 °C. The precipitate was removed by filtration. The filtrate was evaporated, and dissolved in $CHCl_3$. The solution was washed with water, and evaporated. The residue and HOBt (1.9 g, 0.013 mol) was dissolved in 50 mL of DMF, and each 0.013 mol of butanoic acid or benzenepropanoic acid was added. The solution was treated with dicyclohexylcarbodiimide (2.6 g, 0.013 mol) under stirring for 1 day at 0 ºC. The solvent was evaporated under reduced pressure, and the crude compound was obtained. Compounds **1** or **2** were purified by silica gel column chromatography (Wakogel C-200, eluent; chloroform for **1**, and chloroform / ethyl acetate (9:1) for **2**, respectively).

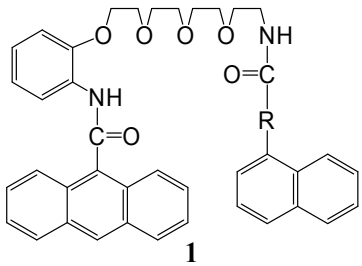
SCHEME 1



Data for characterization of compounds **1** and **2**

1-[2-(9-anthracenecarboxamido)phenoxy]-11-(butanamido)-3,6,9-trioxaundecane ***(1)*** : Yield 47 %. Yellowish oil. ^{1}H-NMR (acetonitrile-d_3) δ (ppm) = 0.86 (-CH_3, m, 3H), 1.52 (C-CH_2-C, m, 2H), 2.01 (CO-CH_2-C, t, 2H), 2.91 (-C-CH_2-O, t, 2H), 3.12 (-C-CH_2-O, t, 4H), 3.15 (-C-CH_2-O, t, 2H), 3.27 (-C-CH_2-O, t, 2H), 3.31 (-C-CH_2-O, t, 2H), 3.60 (-C-CH_2-O, t, 2H), 4.11 (-C-CH_2-O, t, 2H), 6.25 (NH, s, 1H), 7.12 (aromatic, d, 1H), 7.17 (aromatic, t, 1H), 7.21 (aromatic, t, 1H), 7.58 (aromatic, m, 4H), 8.13 (aromatic, d, 2H), 8.17 (aromatic, d, 2H), 8.49 (aromatic, d, 1H), 8.65 (aromatic, s, 1H), 8.83 (NH, s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.8, 167.4, 147.8, 132.1, 131.1, 128.6, 128.39, 128.32, 128.1, 126.7, 125.5, 125.2, 124.6, 122.1, 121.2, 113.2, 70.32, 70.10, 70.06, 69.85, 69.81, 69.26, 39.02, 38.6, 19.1, 13.7. Found : C, 69.76; H, 6.96; N, 4.90%. Calcd. for $C_{33}H_{38}O_6N_2 \cdot 1/2H_2O$: C, 69.82; H, 6.93; N, 4.93%.

1-[2-(9-anthracenecarboxamido)phenoxy]-11-(benzenepropanamido)-3,6,9-trioxaundecane ***(2)*** : Yield 45 %. Yellowish oil. ^{1}H-NMR (acetonitrile-d_3) δ (ppm) = 2.32 (CO-CH_2-C, t, 2H), 2.82 (C-CH_2-C, t, 2H), 2.89 (-C-CH_2-O, t, 2H), 3.13 (-C-CH_2-O, t, 2H), 3.14 (-C-CH_2-O, t, 4H), 3.20 (-C-CH_2-O, t, 2H), 3.29 (-C-CH_2-O, t, 2H), 3.58 (-C-CH_2-O, t, 2H), 4.09 (-C-CH_2-O, t, 2H), 6.26 (NH, s, 1H), 7.10 (aromatic, d, 1H), 7.13 (aromatic, q, 4H), 7.18 (aromatic, t, 1H), 7.57 (aromatic, m, 4H), 8.12 (aromatic, m, 4H), 8.47 (aromatic, s, 1H), 8.64 (aromatic, s, 1H), 8.81 (NH, s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.1, 167.7, 148.1, 141.2, 132.4, 131.4, 128.8, 128.6, 128.5, 128.4, 128.1 127.0, 126.3, 125.8, 125.5, 124.9, 122.4, 121.5, 113.5, 70.61, 70.37, 70.32, 70.11, 70.00, 69.53, 69.53, 39.3, 38.5, 31.9. Found: C, 72.28; H, 6.58; N, 4.45%. Calcd. for $C_{36}H_{38}O_6N_2 \cdot 1/2H_2O$: C, 72.48 H, 6.56; N, 4.45%.



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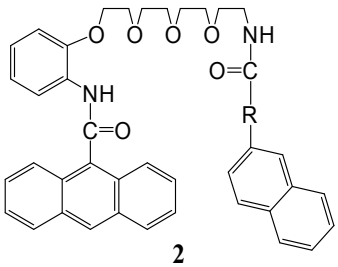


2

Evaluation of Mg^{2+} and Ca^{2+} concentrations in mixture of these ions

The concentrations of Mg^{2+} and Ca^{2+} in a sample solution can be determined by the measurement of fluorescence intensities at two different wavelengths, according to following equations.

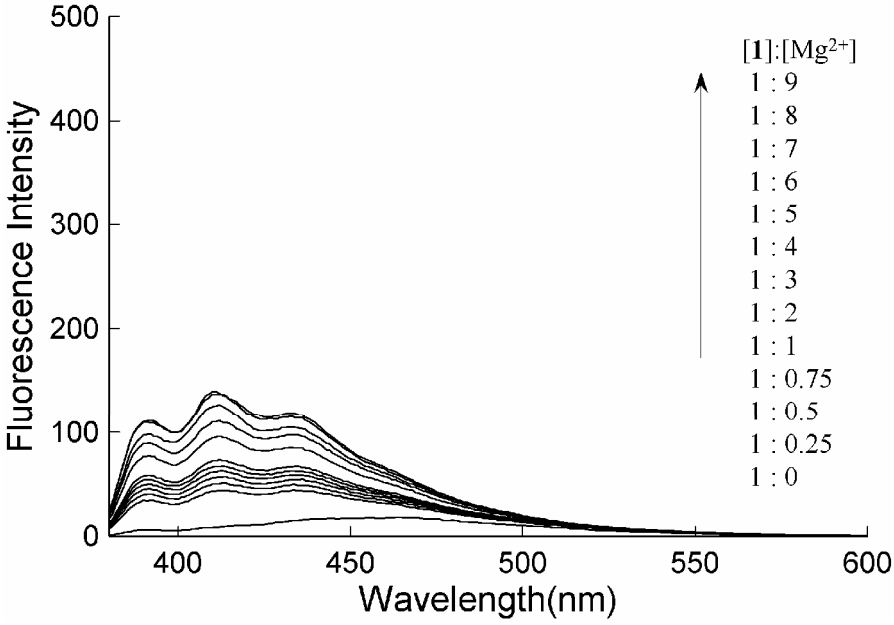
$I(\text{obs; } 394) \simeq \eta(\text{Ca; } 394)\,[CA^{2+}] + \eta(\text{Mg; } 394)\,[Mg^{2+}]$
$I(\text{obs; } 440) \simeq \eta(\text{Ca; } 440)\,[CA^{2+}] + \eta(\text{Mg; } 440)\,[Mg^{2+}]$

$[Ca^{2+}] = \{ I(\text{obs; } 440) \times \eta(\text{Mg; } 394) - I(\text{obs; } 394) \times \eta(\text{Mg; } 440) \} / \{ \eta(\text{Ca; } 440) \times \eta(\text{Mg; } 394) - \eta(\text{Ca; } 394) \times \eta(\text{Mg; } 440) \}$

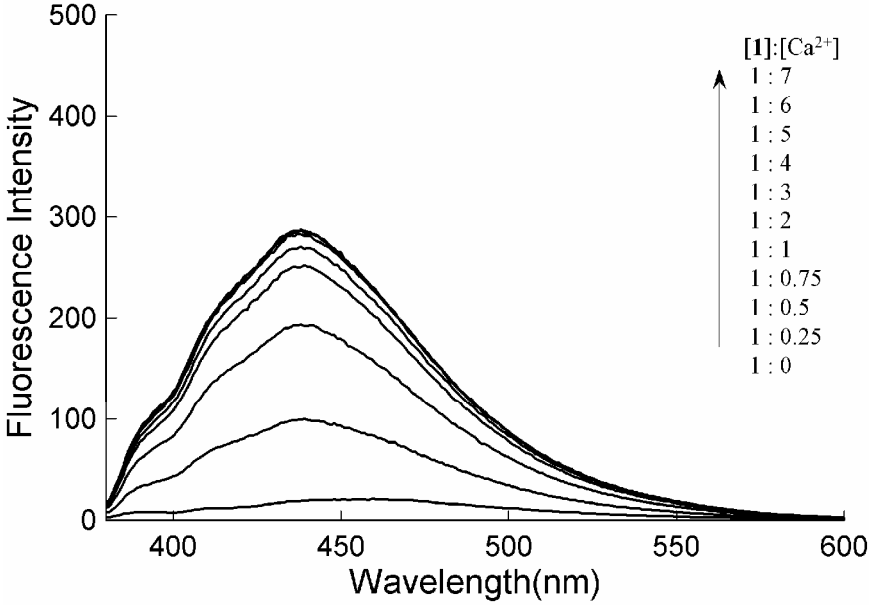
$[Mg^{2+}] = \{ I(\text{obs; } 394) \times \eta(\text{Ca; } 440) - I(\text{obs; } 440) \times \eta(\text{Ca; } 394) \} / \{ \eta(\text{Ca; } 440) \times \eta(\text{Mg; } 394) - \eta(\text{Ca; } 394) \times \eta(\text{Mg; } 440) \}$

Here, η(Mg; 394) and η(Mg; 440) are fluorescence intensity coefficients for the concentration of Mg^{2+} complex at 394 nm and 440 nm , respectively.
η(Ca; 394) and η(Ca; 440) are fluorescence intensity coefficients for the concentration of Ca^{2+} complex at 394 nm and 440 nm , respectively.

I(obs; 394) and I(obs; 440) are observed intensities at 394 nm and 440 nm, respectively, for the sample solution.



< Fluorescence spectra of **1** and its Mg^{2+} complexes >



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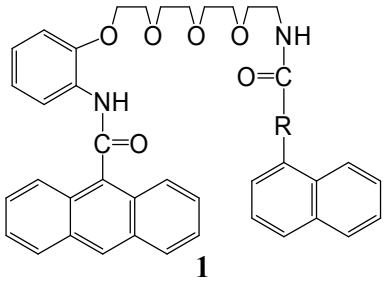

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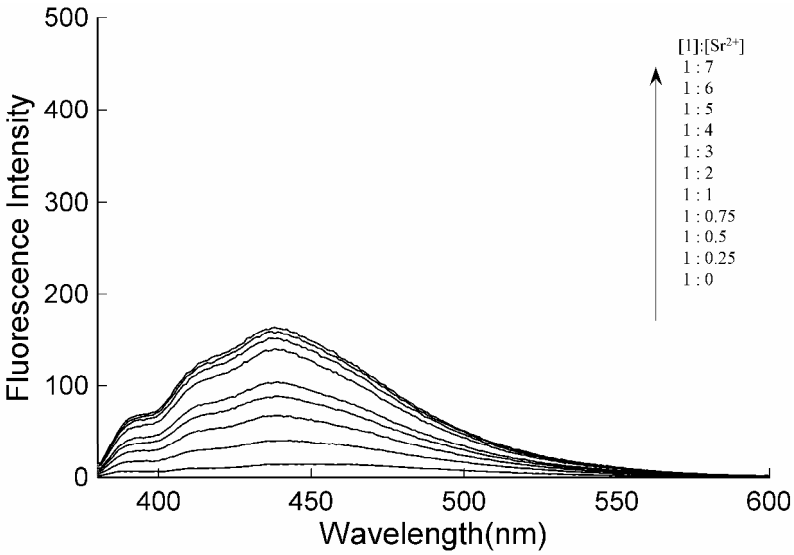

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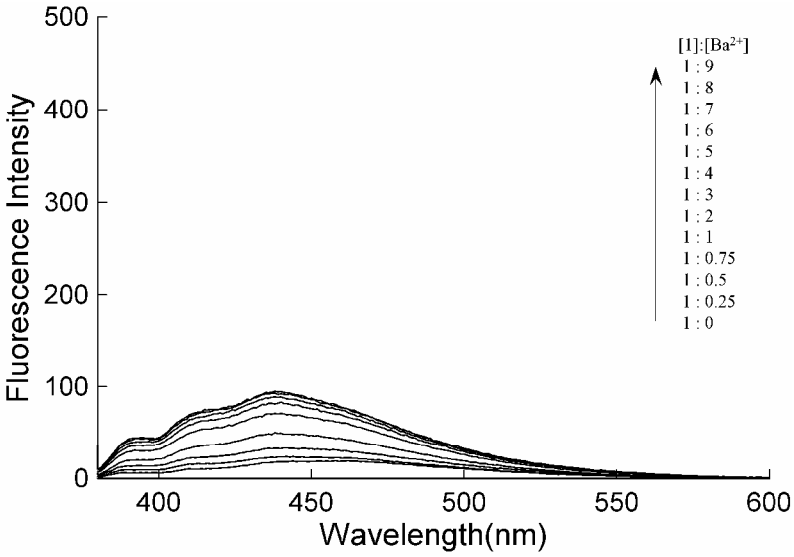

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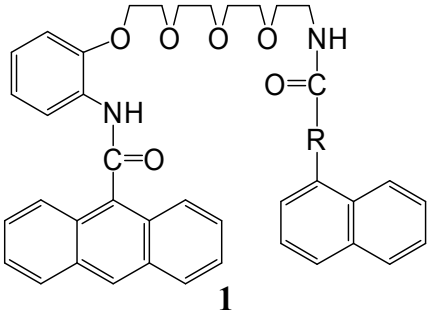

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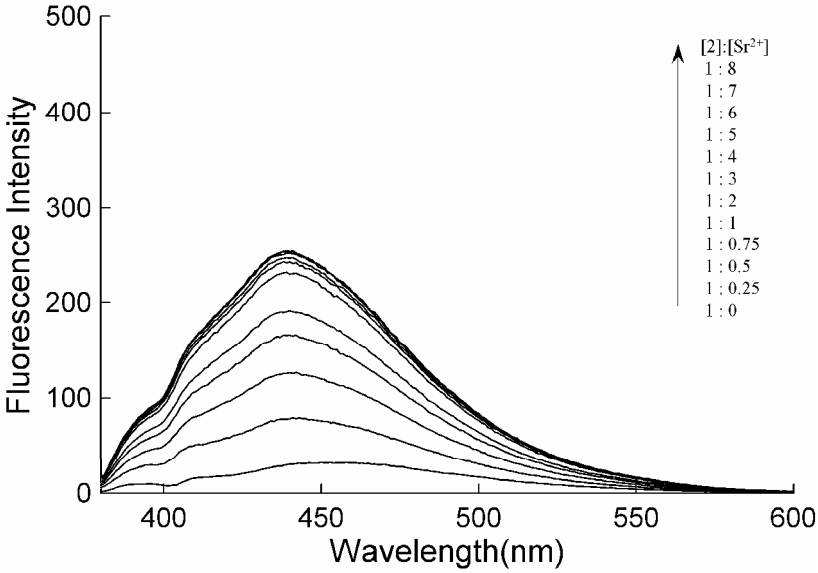

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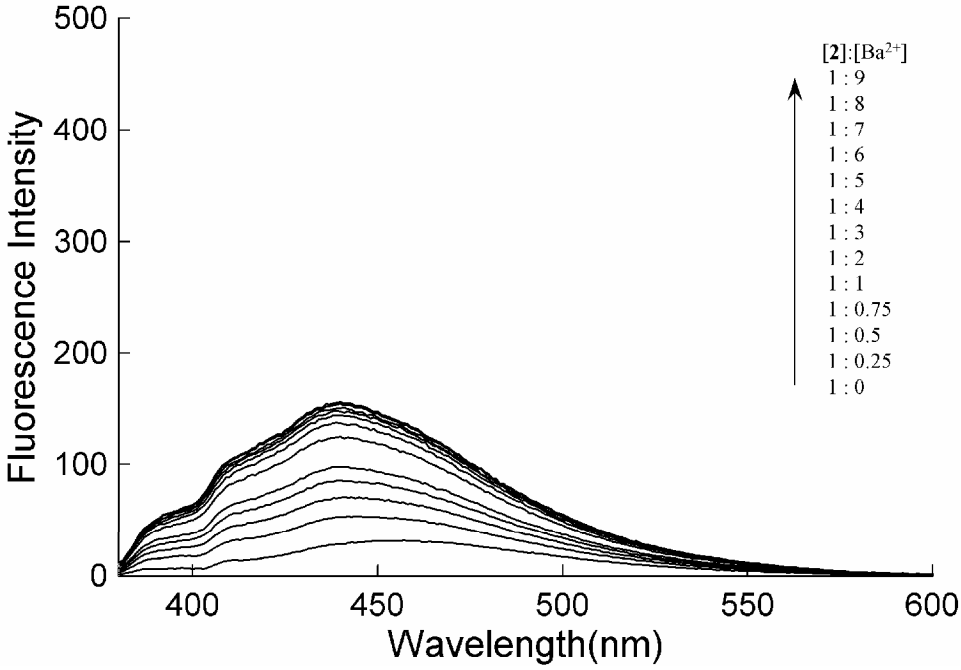

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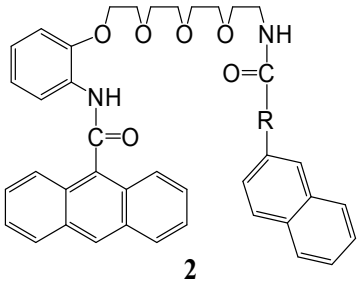

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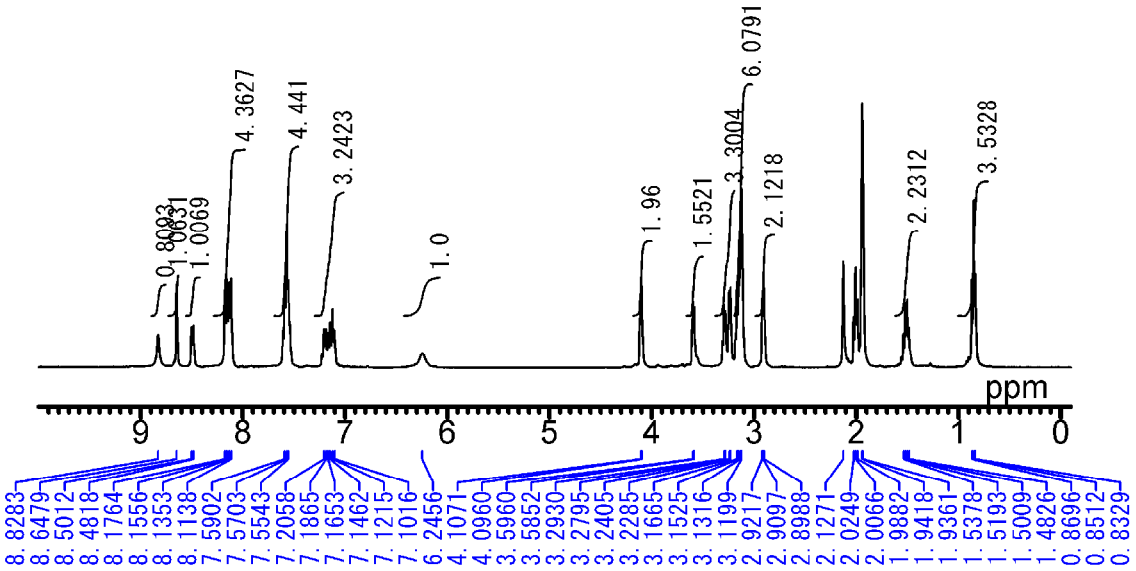
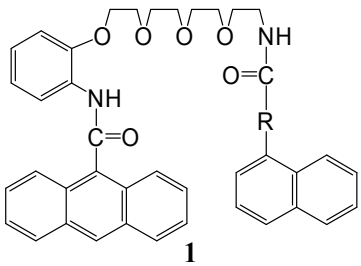


< ^{1}H NMR of compound **1** >



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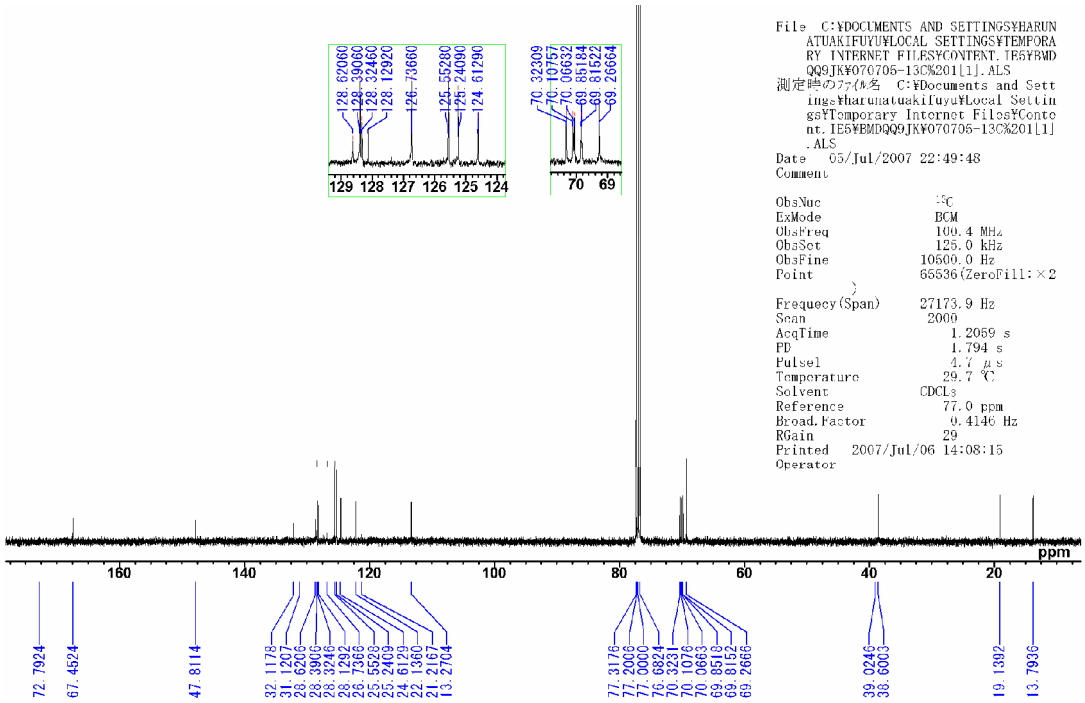

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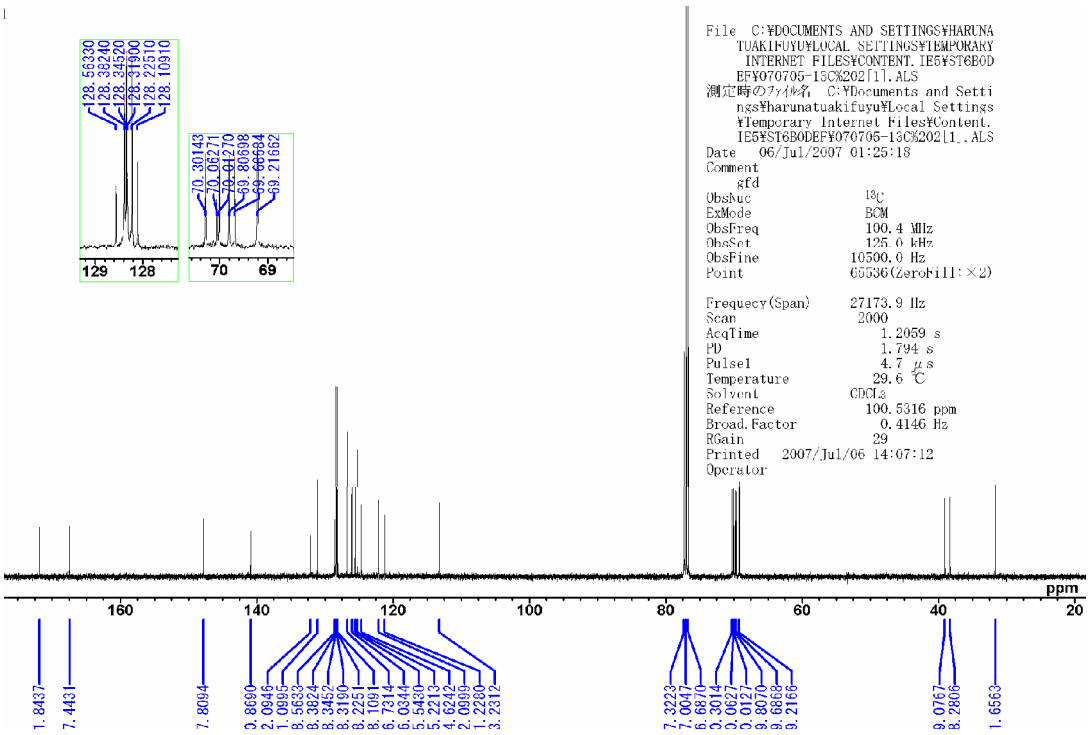

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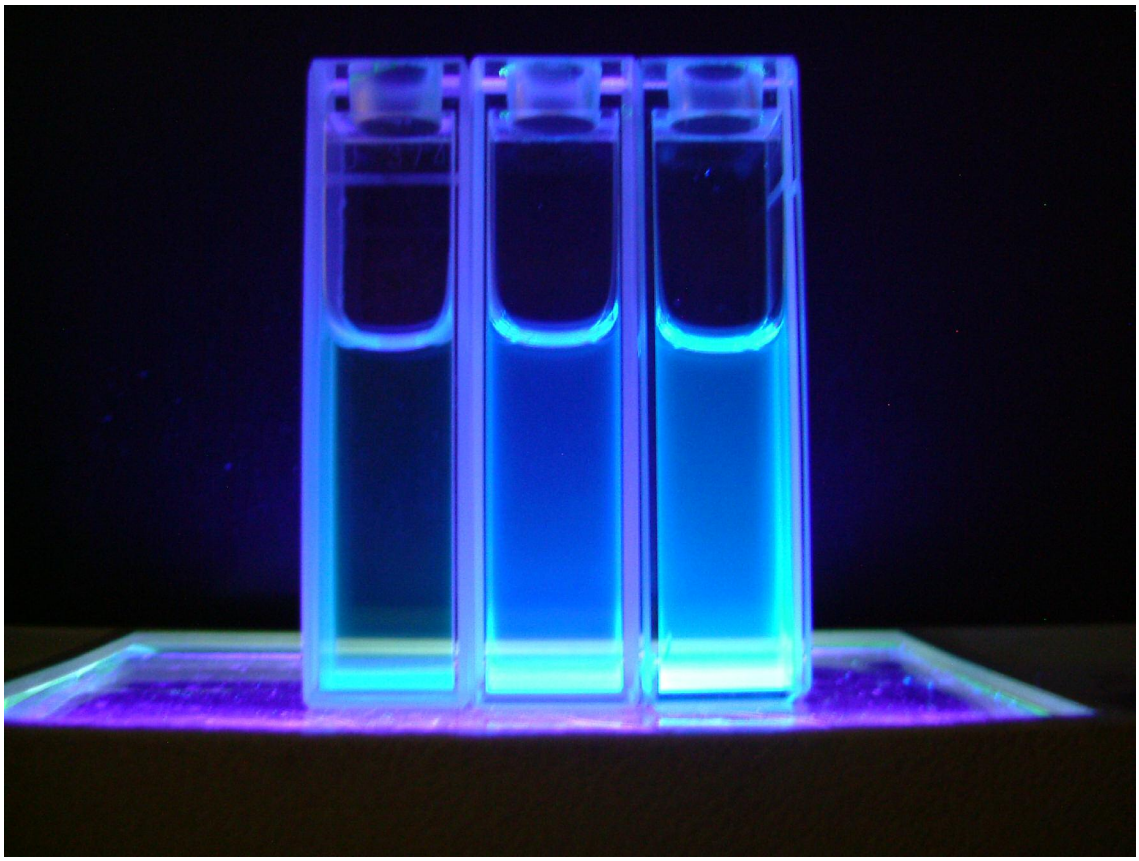
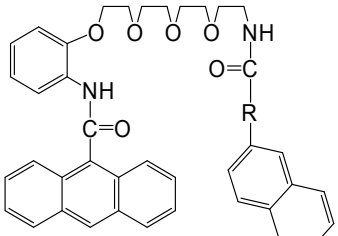


Figure. Fluorescence emission colors of free **2** (left), **2**·Mg^{2+} (center) and **2**·Ca^{2+} (right).



2

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Curve fitting plot for fluorescence intensity vs. [metal]:[ligand] in the 1·Ca^{2+} complex

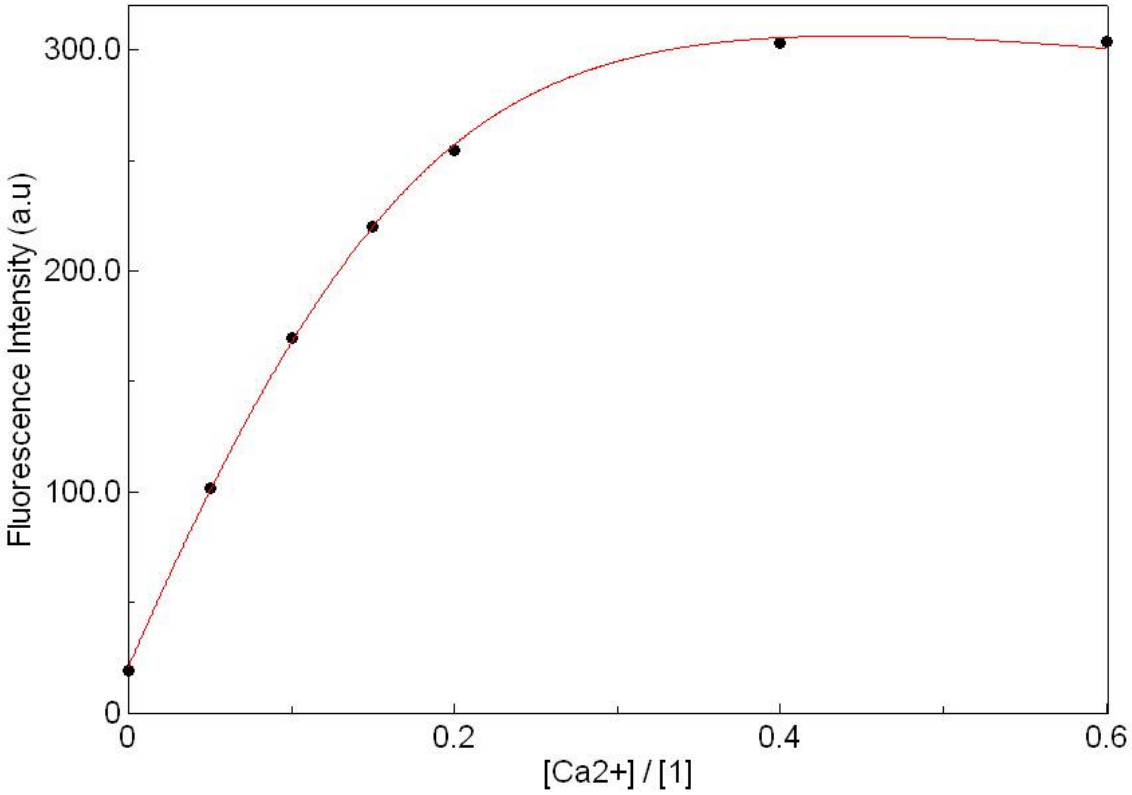

Figure. Excitation wavelength : 363 nm. Fluorescence wavelength : 438 nm. [**1**] = 1 × 10^{-5} mol/dm^3.