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Highly efficient and selective turn-off quenching of ligand-sensitized luminescence from europium imidazo[4,5-*f*]-1,10-phenanthroline complex by fluoride ion

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ABSTRACT

A smart fluoride sensitive luminescence probe based on 1:2 complex of europium(III) with 2-(2-hydroxyphenyl)imidazo[4,5-*f*]-1,10-phenanthroline was prepared. The emission of europium ions via photosensitization of the ligand was completely quenched by addition of 2 equiv. of fluoride ions in DMSO. Spectroscopic analyses proved that the imidazolyl NH of the ligand was hydrogen-bonded with additive fluoride to form the 1:1 complex, leading to suppression of the photosensitization.

1. Introduction

Since luminescent lanthanide complexes show unique photophysical properties such as long lifetimes, sharp emission peaks and large Stokes shifts, the typical rare earth complexes (especially europium and terbium complexes), have been considered to be useful in bioassays, electroluminescent area and laser devices [1–4]. Common lanthanide ions have very small absorption coefficients in the ultra-violet, visible and near-infrared regions, so strongly absorbing organic ligands are necessary for light-harvesting in order to attain efficient photoluminescence. Lately, rare earth complexes have been considered to be quite critical for sensing various anions in terms of their unique optical properties [5–12]. 1,10-Phenanthroline is well known as the ligand of luminescent lanthanide complexes, which can sensitize europium ions effectively [3]. In the present study, we report the synthesis and characterization of europium complex with 2-(2-hydroxyphenyl)-imidazo[4,5-*f*]-1,10-phenanthroline (**1**) which is easily available and fairly stable (Fig. 1). It is interesting to find that the synthetic europium compound exhibited red-colored emission due to efficient sensitization by the ligand, similarly to the corresponding intact 1,10-phenanthroline ligand [13]. More importantly, the present complex which bears double NH and OH as hydrogen bond donors per ligand is of interest in the same way as a well-known calixpyrrole [14]. Addition of fluoride anion as a hydrogen bond acceptor suppressed the europium luminescence selectively.

2. Experimental

2.1. General

All starting materials were obtained from commercial suppliers and used as received. ^{1}H and ^{19}F NMR spectra were recorded with JOEL AL600 (600 and 565 MHz) at 298 K using trimethylsilane as an internal standard ($\delta = 0$ ppm) and trifluoroacetic acid as an external standard ($\delta = -77$ ppm), respectively. Visible and fluorescence spectra were measured on Hitachi U-3500 and F-4500 spectrometers, respectively. TOF-MS and FAB-HRMS were measured at Shimadzu Axima-CFR plus and JEOL GCmate II apparatus, respectively.

2.2. Synthesis of 2-(2-hydroxyphenyl)imidazo[4,5-f]-1,10-phenanthroline (1)

1,10-Phenanthroline-5,6-dione (100 mg, 0.48 mmol) which was prepared as reported in the literature [15,16] was mixed with ammonium acetate (1.1 g, 14.4 mmol), then dissolved in glacial acetic acid (3 ml). During stirring, 2-hydroxybenzaldehyde (58.6 mg, 0.48 mmol) in acetic acid (2 ml) was added to the above mixture. The solution was heated to 90 °C for 3 h and quenched by water (50 ml). An aqueous ammonium solution (35%, 5 ml) was

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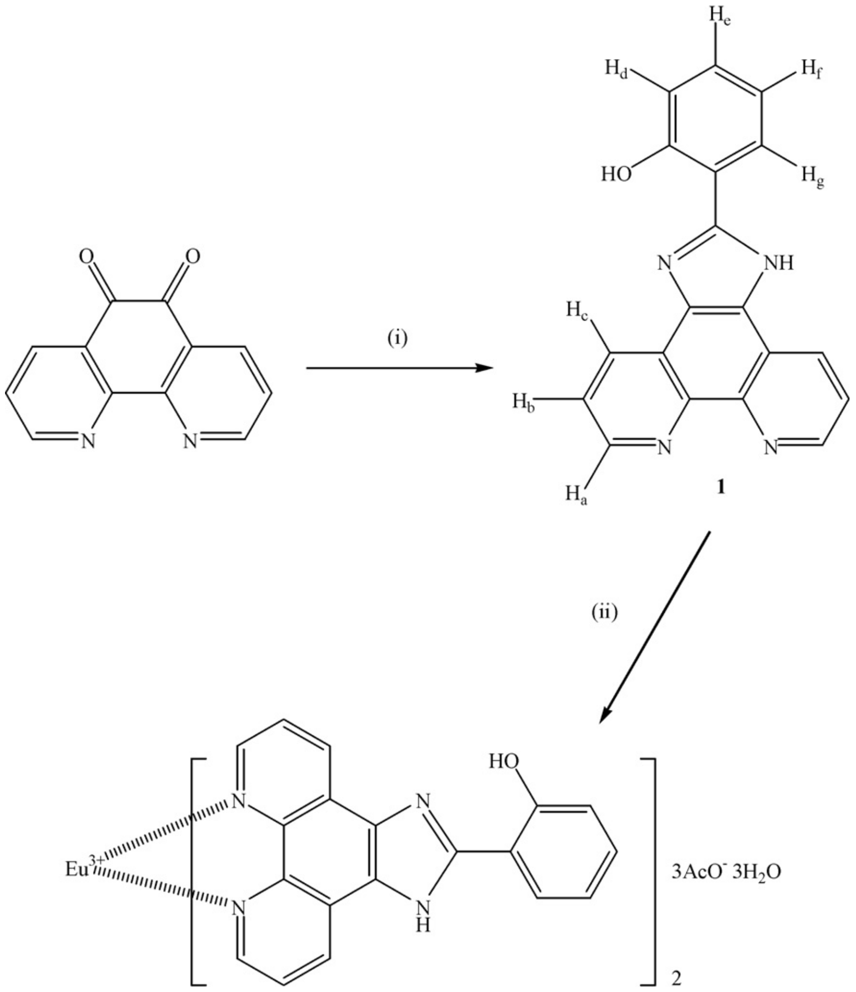


Fig. 1. Synthesis of europium(III) complex of 2-(2-hydroxyphenyl)imidazo[4,5-*f*]-1,10-phenanthroline (**1**); (i) 2-HOC_6H_4CHO, $AcONH_4$, AcOH, 90 °C; (ii) $Eu(OAc)_3 \cdot 4H_2O$, EtOH, reflux.

added to neutralize the solution to pH 7. The precipitate was collected and washed with water. The crude product was dried in vacuo overnight. Further purification was performed by flash column chromatography with alumina (aluminum oxide 90, deactivated neutral, 70–230 mesh) with CH_2Cl_2/MeOH = 100/1 as eluted solvents. The second band was collected to give the titled compound (62.8 mg, 42%) as a yellow solid [17]: ^1H NMR (DMSO-d_6) δ = 13.9, 12.9 (each 1H, br, NH, OH), 9.05 (2H, d, J = 4.8 Hz, H_a), 8.91 (2H, d, J = 4.8 Hz, H_c), 8.25 (1H, d, J = 4.0 Hz, H_g), 7.91 (2H, m, H_b), 7.41 (1H, t, J = 5.6 Hz, H_e), 7.10 (2H, m, H_d, H_f); MS (TOF) found: *m*/*z* 313.3 (MH^+); HRMS (FAB) found: *m*/*z* 313.1089 (MH^+), calcd for $C_{19}H_{13}N_4O$ 313.1089.

2.3. Synthesis of [Eu(**1**)$_2$(CH_3COO)$_3$]·3H_2O

Compound **1** (18.7 mg, 0.06 mmol) was dissolved in ethanol (10 ml), to which $Eu(CH_3COO)_3 \cdot 4H_2O$ (13.3 mg, 0.03 mmol) was added. The whole mixture was refluxed overnight and cooled down to room temperature. The resulting precipitate was collected and washed with water twice to give the titled complex (27 mg, 90%) as a pale yellow powder: IR ($CHCl_3$) υ = 3629, 3440 (br), 2945, 2837, 1600, 1446, 1332, 1074, 1016, 850, 726 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 8.95 (4H, br, H_a), 8.85 (4H, br, H_c), 8.30 (2H, br, H_g), 7.72 (4H, br, H_b), 7.18 (2H, br, H_e), 7.10 (4H, br, H_d, H_f); EA found: C, 52.60; H, 3.77; N, 10.81%, Anal. Calcd for $C_{44}H_{39}EuN_8O_{11}$(=[Eu(1)$_2$(CH_3COO)$_3$]·3H_2O): C, 52.44; H, 3.90; N, 11.12%. No useful ESI-MS data for clarification of the 1:2 species in a solution were obtained due to its instability even in the present soft ionization.

2.4. Synthesis of 2-phenyl-imidazo[4,5-f]-1,10-phenanthroline (**2**)

Similar to the synthesis of **1**, the condensation using benzaldehyde gave the titled compound (50 mg, 53%) as a yellow solid [18]: ^1H NMR (DMSO-d_6) δ = 9.03 (2H, d, J = 6.4 Hz, H_a), 8.94 (2H, d, J = 6.4 Hz, H_c), 8.30 (2H, d, J = 7.2 Hz, H_d), 7.85 (2H, m, H_b), 7.62 (2H, t, J = 7.2 Hz, H_e), 7.52 (1H, t, J = 7.2 Hz, H_f); MS (TOF) found: *m*/*z* 297.3 (MH^+); HRMS (FAB) found: *m*/*z* 297.1136 (MH^+), calcd for $C_{19}H_{13}N_4$ 297.1140.

3. Results and discussion

Ligand **1** bearing a phenanthroline ring adopted the coordination mode with a europium ion in ethanol to give a pale yellow complex. The structure of the resulting 1:2 complex of Eu(III) with **1** as shown in Fig. 1 was supported by elementary analysis. A similar 1:2 complex (not 1:3) was already reported in the reaction of europium acetate with unsubstituted phenanthroline [19]. [Eu(1)$_2$(CH_3COO)$_3$]·3H_2O was dissolved in dimethylsulfoxide (DMSO, 5×10^{-6} M) to give a colorless solution with three UV maxima at 318, 337 and 354 nm (solid line of Fig. 2). When 2 equiv. of tetrabutylammonium fluoride ($[Bu_4N]^+F^-$) were added to the solution, the three absorption peaks increased dramatically, and concomitantly, a new broad band centered at around 425 nm

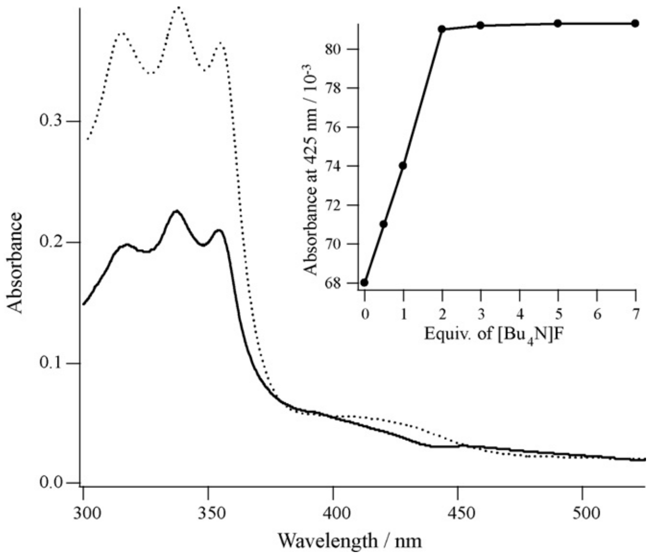


Fig. 2. UV–vis spectra of europium complex (5×10^{-6} M) in DMSO before (solid line) and after addition of 2 equiv. of $[Bu_4N]F$ (dotted line). Inset: absorbance change at 425 nm as a function of fluoride ion concentration.

appeared (see dotted line of Fig. 2). After addition of the salt, the solution was pale yellow colored due to the latter band at the visible region. Addition of the other anions Cl^-, Br^-, I^- and ClO_4^-, caused small variations compared with the original spectrum without any additive (Fig. S1). The phenomenon would be ascribable to preferable binding of F^- to ligand **1** because a fluoride ion bears with a high charge density, small atomic diameter and strong hydrogen bonding capability. The titration of F^- into europium complex in DMSO altered the solution from colorless to pale yellow, and the absorbance at 425 nm increased until the addition of 2 equiv. of $[Bu_4N]^+F^-$ to reach a constant value over the 2 equiv. (inset of Fig. 2). Addition of more than 2 equiv. of fluoride caused no further change in the UV–vis spectra, showing that one europium complex bound two fluoride ions through the 1:1 strong binding of ligand **1** with F^-. In order to fully confirm this issue, we measured the absorption spectra of free ligand **1** in DMSO without and with $[Bu_4N]^+F^-$. Similar changes in absorption bands were observed (Fig. S2), indicating the 1:1 binding of **1** with F^-. Likewise, the broad band appeared in the range of 400–450 nm was closely related to the interactions of the pure organic ligand **1** with fluoride anion.

Due to the paramagnetic effect of the europium complex that made the proton signal somewhat broadened, we had to use free ligand **1** instead of Eu-complex to check the formation of its adduct with F^- by way of NMR in DMSO-d_6 at room temperature (Fig. 3). After addition of 1 equiv. of fluoride ion, the proton signals of the NH and OH entirely disappeared, which is in good agreement with the formation of strong hydrogen-bonded complexes with F^-. Moreover, the dehydroxylated compound **2** (Scheme 1) was complexed with 1 equiv. of fluoride anion in DMSO from UV–vis spectral analyses (Fig. S3). These results showed that the NH group of **1** probably plays a primary role in this complexation process but the contribution from the OH still could not be ruled out. As shown in Fig. 3a and b, all the aromatic chemical shifts of H_a to H_f were shifted to an upfield region except a small downfield shift of H_g by the addition of 1 equiv. of fluoride. More than 1 equiv. of F^- caused no further change in any of the proton signals on the aromatic ring, which firmly proved that **1** was bound to a fluoride ion at 1:1 stoichiometry. Similar NMR experiments were also performed with the addition of Cl^-, Br^-, I^- and ClO_4^-, but **1** caused no change in any proton (data not shown), indicating that only fluoride ions triggered the drastic change of free ligand **1**, which was consistent with the UV–vis results mentioned above. Addition of an excess amount (around 5 equiv.) of fluoride has brought a triplet signal corresponding to HF_2^- around 16.1 ppm (Fig. S4), again showing that fluoride anions interacted with the NH group of **1**.

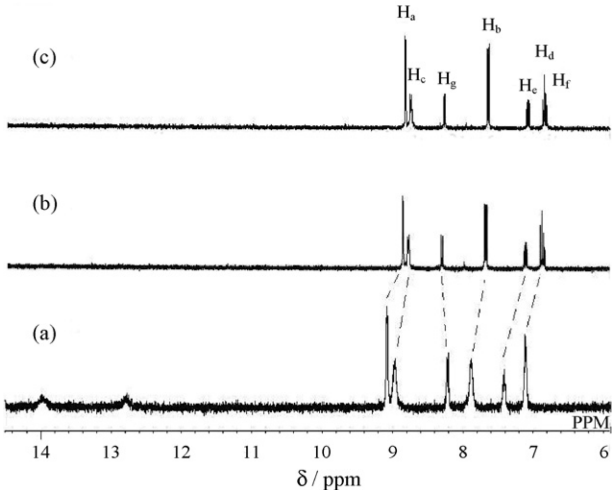
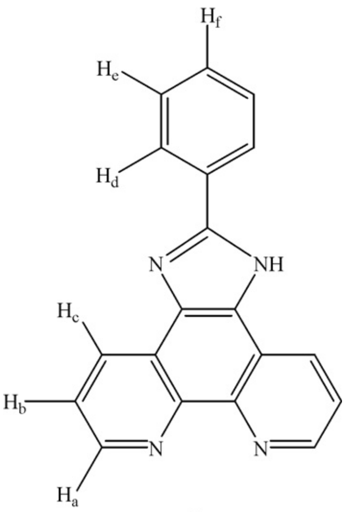


Fig. 3. ^1H NMR spectra measured by titration of a DMSO-d_6 solution of pure **1** (1 mM) with 0 equiv. (a), 1 equiv. (b) and 4 equiv. of $[Bu_4N]F$ (c).

Furthermore, the association of **1** with F^- in DMSO-d_6 was studied using NMR technique. In Job's plot, the upfield shifts of δs in **1** reached a maximum at the mole fraction of **1** = 0.5 (Fig. S5), confirming the formation of 1:1 complex between **1** and F^-. Based on the changes of δs in **1** with 0–8 equiv. of $[Bu_4N]^+F^-$, the association constant K_a of the **1** with $[Bu_4N]^+F^-$ was calculated by non-linear least squares fit with the 1:1 binding model [20], giving $K_a = 2.2 \times 10^5$ M^{-1}. The value shows high selectivity compared with the reported data [21,22]. To further prove the interactions between **1** and fluoride ions, ^{19}F NMR spectra of $[Bu_4N]F$ in DMSO-d_6 were measured before and after the addition of **1**. Compound **1** triggered the shift of the fluoride peak from −72.2 to −73.2 ppm as a result of the hydrogen bonding formation (Fig. S6).

When a DMSO solution of $[Eu(\mathbf{1})_2(CH_3COO)_3]\cdot 3H_2O$ (5×10^{-6} M) was irradiated with light of 370 nm, narrow emission peaks were observed at the visible region and assigned to transitions between the excited $^5D_0$ level and various J-levels of the ground state ^7F_J (J = 1, 2, 3 and 4) at 590 nm ($^5D_0 \rightarrow {}^7F_1$), 614 nm



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Scheme 1.

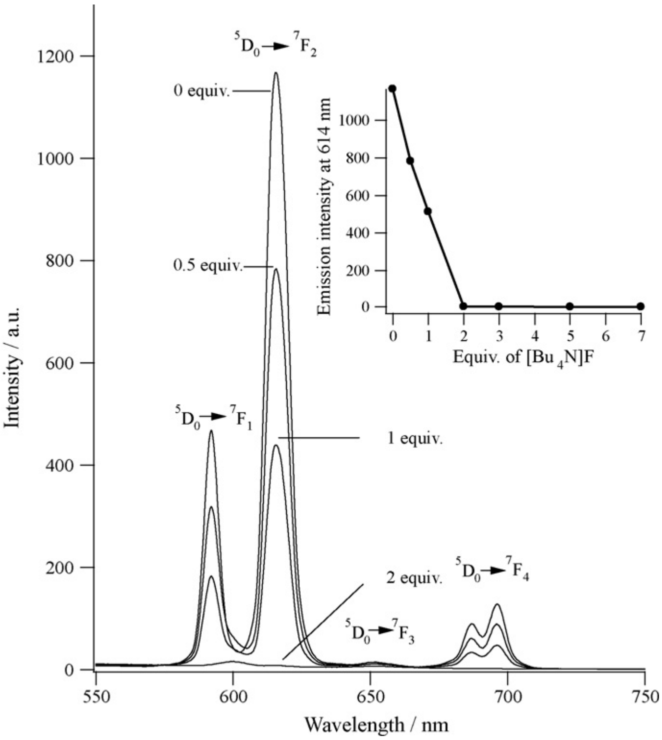

Fig. 4. Emission spectra of europium complex (5×10^{-6} M) in DMSO with 0, 0.5, 1 and 2 equiv. of [Bu$_4$N]F (excitation = 370 nm). Inset: emission intensity at 614 nm as a function of fluoride ion concentration.

($^5D_0 \rightarrow {}^7F_2$), 650 nm ($^5D_0 \rightarrow {}^7F_3$) and 686/696 nm ($^5D_0 \rightarrow {}^7F_4$) (Fig. 4). The 370-nm light selectively excited ligand **1** in the complex, so the emission from the Eu(III) center was attributed to energy transfer from the photoexcited ligand to the metal center. The excitation spectra at 614-nm emission were observed covering from 250 to 450 nm where **1** harvested light mainly in this region (Fig. S7). The quantum yield of emission from the europium at 370-nm excitation was determined to be 6.7%. This value was lower than the reported data of an europium complex with phenanthroline and thenoyltrifluoroacetonate [23], indicating that photosensitization of ligand **1** to Eu center in the complex was less efficient because of unsaturated coordination around this center.

The most intense emission peak was ascribable to the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ at 614 nm. Remarkable reduction of the emission was seen on addition of fluoride ions. About a 30% quenching in the intensity of the emission peak at 614 nm was found after the addition of 0.5 equiv. of [Bu$_4$N]F. Upon successive addition of F$^-$ to 2 equiv., the red luminescence continued to diminish until it had completely disappeared. The same dramatic luminescence change can be easily observed by the naked eye under excitation at 254-nm light (Fig. 5). The variation observed in the emission spectra by titration of more than 2 equiv. of [Bu$_4$N]F was insignificant, which was very similar to the results of UV–vis measurements. The results clearly supported that a 1:2 hydrogen-bonded complex formed between the europium complex and [Bu$_4$N]F and that the 1:2 adduct was a non-luminescent species. Analogous experiments were conducted with Cl$^-$, Br$^-$, I$^-$ and ClO$_4^-$; 50 equiv. titration of the corresponding [Bu$_4$N]$^-$ salts were examined in their emission spectra (Fig. S8). As expected from the above UV–vis absorption and ^{1}H NMR measurements showing that no hydrogen-bonding formation was detected by these anions, the influence of the emission of europium ions was relatively low even in the presence of 50 equiv. The largest luminescence reduction brought by ClO$_4^-$ was at most 20%. Accordingly, the UV–vis absorption and emission investigations confirmed that the present europium complex can be applied as a chemical sensor specific for fluoride anions.

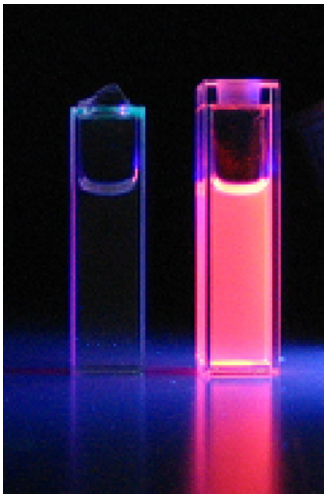

Fig. 5. Europium complex (5×10^{-6} M) in DMSO with 0 equiv. (right) and 2 equiv. of [Bu$_4$N]F (left) excited at 254-nm UV light.

In general, the photosensitization path within a molecular lanthanide-containing complex is predominant through the triplet state of ligand (T*) and sometimes by way of the singlet state of ligand (^{1}S*) [24,25]. The emission bands of **1** at around 450 nm were reduced gradually upon the addition of [Bu$_4$N]F (Fig. S9), showing that fluoride anions would invoke deactivation of S* directly towards the ground state. Another point to be stressed here is that the formation of intermolecular hydrogen-bonding might impede the intersystem crossing process (S* → T*) to suppress the population of T*. Therefore, no more luminescence from europium ions was observed through intramolecular energy transfer from the excited state (T* and/or S*) of ligand **1** after addition of >2 equiv. of fluoride ions in DMSO.

4. Concluding remarks

In this report we developed a new and reliable strategy for a luminescent chemical sensor specific to fluoride ion. Upon the addition of F$^-$, the unique red emission peak of the present europium complex was significantly reduced and completely quenched by 2 equiv. of F$^-$ through the hydrogen-bonding interaction between ligand **1** and F$^-$. It is worth pointing out that the addition of excess amounts of Cl$^-$, Br$^-$, I$^-$ and ClO$_4^-$ create some variation of emission bands of europium ions but no extraordinary change such as being fully *turned off* like fluoride ions can be observed. Moreover, we found that the replacement of ligand **1** by **2** made the energy transfer from photoexcited **2** to europium center less efficient, probably due to free rotation of the phenyl group on the phenanthroline ring which would impact the excited energy levels of the peripheral ligands [26]. Therefore, we consider that the OH group in **1** plays an important role in fixing the planar conformation of the ligand which can facilitate the energy migration to metal ions. Although the current experiments were performed in DMSO, our findings will be further developed as unique lanthanide based receptors for future practical use. The present europium complex of **1** immobilized on inorganic materials such as SiO$_2$ and TiO$_2$ will have potentially important application as solid chemosensors used in the heterogeneous solid–liquid phase.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.05.024.

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