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A Molecular Switch with pH-Controlled Absolutely Switchable Dual-Mode Fluorescence

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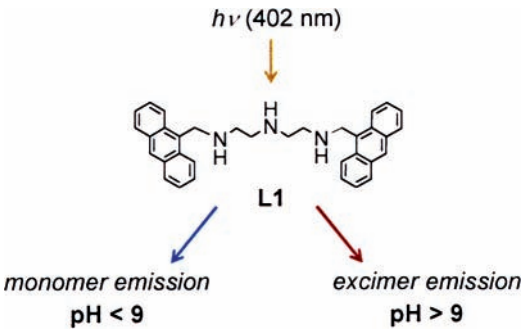
ABSTRACT



A simple-structured molecule (L1) bearing anthracene fragments at both ends of diethylenetriamine chain behaves as a fluorescent molecular switch with pH-controlled absolutely switchable dual-mode fluorescence in water; each mode consists of monomer (pH <9) and excimer (pH >9) emissions.

Design and synthesis of fluorescent molecules with a switch function is an area of intense research activity and tremendous potential significance to the field of sensor device fabrication.[1] A large number of molecular switches have so far been synthesized based on systems whose emission properties can be modulated by external inputs, such as pH,[2] temperature,[3] light,[4] redox potential,[5] and metal ions.[6] However, most of the systems show "on/off switching" function of single fluorescence emission. Development of molecular switch, enabling a control of multiple-mode fluorescence, is of current interest.[7]

Herein, we describe a new member of this family, **L1** (Figure 1), which shows "absolute switching" function of

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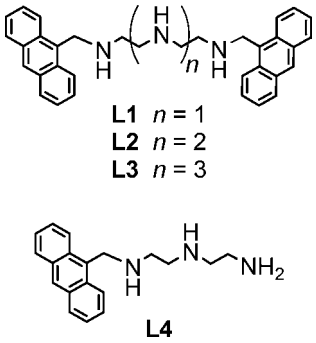

Figure 1. Structure of polyamines bearing anthracene fragments, **L1**−**L4**.

dual-mode fluorescence in water by pH input. This is the first system enabling the absolute dual-mode switching. This molecule is made simply by attaching anthracene fragments at both ends of the diethylenetriamine chain.[8] The switching function involves a pH-controlled bending movement of the polyamine chain leading to the formation of unexpected intramolecular charge transfer (ICT) complex in the ground state, via a π-stacking interaction of two fluorophores and solvation of H_2O molecules.

As shown in Figure 2A (λ_{ex} = 402 nm), **L1** shows a distinctive fluorescence at 400−500 nm in water with acidic-neutral pH (<9), which is attributable to a monomer emission from the excited anthracene. As observed for related anthracene-conjugated polyamines,[9] the intensity of the monomer emission decreases with the progress of deprotonation of **L1**. This is because the unprotonated amines are efficient electron-transfer quenchers of the excited anthracene.[1g] This trend is illustrated in Figure 2B, where the emission intensity monitoring at 416 nm is plotted against pH (blue symbols) together with the mole fraction distribution of the different protonated species (dotted line) of **L1**, which is calculated from the protonation constants determined potentiometrically.[10] The fully protonated form of **L1** (H_3**L1**$^{3+}$ species)

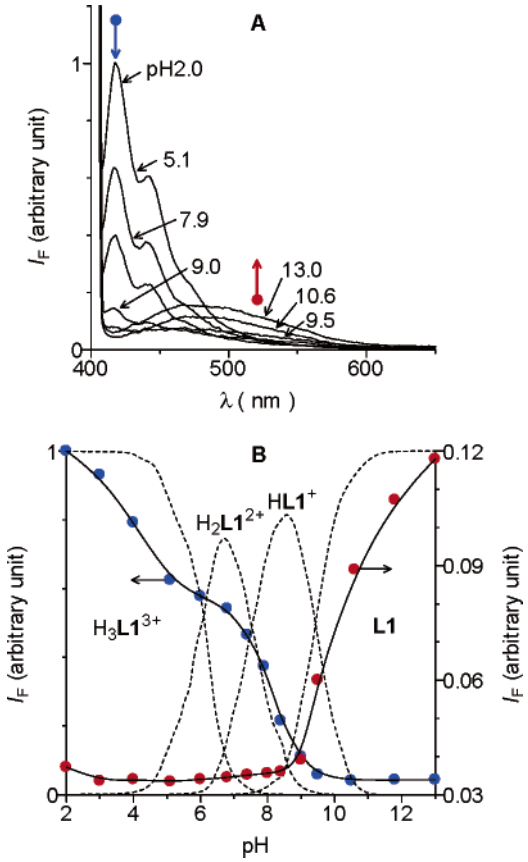

Figure 2. (A) pH-dependent change in the fluorescence spectra (λ_{ex} = 402 nm) of **L1** (70 μM) in aqueous NaCl (0.15 M) solution at 298 K. (B) Mole fraction distribution of the protonation states of **L1** (dotted line) and intensity of the fluorescence emissions at λ_{em} = 416 nm (blue symbols) and 520 nm (red symbols).

exhibits the most intense emission. Partial emission quenching takes place for H_2**L1**$^{2+}$ species, and total quenching occurs upon further removal of protons from the H_2**L1**$^{2+}$.

The most remarkable feature of the emission spectra of **L1** is the presence of the red-shifted and nonstructured band at 500−600 nm (Figure 2A). The plots of the intensity of this excimer-like emission monitored at 520 nm against pH (Figure 2B, red symbols) demonstrate that this emission appears at pH >9, where fully unprotonated **L1** species exist predominantly, and the emission intensity increases with an increase in the quantity of the **L1** species. It is noteworthy that, at this pH range, the monomer emission is completely absent. These indicate that **L1** switches the dual fluorescence absolutely at pH 9 as a boundary condition.

The excimer-like emission does not appear in the case of **L4** containing a single anthracene unit (Figure S10[11]). This excludes the possibility of formation of an intramolecular charge transfer (ICT) complex between the unprotonated amine and the excited anthracene.[12] The red-shifted emission

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(10) Potentiometric measurements were carried out in aqueous NaCl (0.15 M) solution at 298 K. The program HYPERQUAD (Sabatini, A.; Vacca, A.; Gans, P. *Coord. Chem. Rev.* **1992**, *120*, 389−405.) was used for determination of the protonation constants. The stepwise protonation constants calculated for **L1**: log K(H**L1**/H·**L1**) = 9.45, log K(H_2**L1**/H**L1**·H) = 7.55, and log K(H_3**L1**/H_2**L1**·H) = 6.01.

(11) See the Supporting Information.

(12) Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, *9*, 393−396.

of **L1** is therefore due to an excimer formed via an association of two anthracene units situated at the ends of the polyamine chain. The excimer emission is only observed for the **L1** species, where neither the fully protonated species (H_3**L1**$^{3+}$) nor the species with lower protonation degrees (H_2**L1**$^{2+}$ and H**L1**$^{+}$) yields such emission (Figure 2B). These absences can be ascribed to a large electrostatic repulsion of the protonated amines, which suppresses the required bending movement of the polyamine chain for the association of two fluorophores, as described for related polyamines.[7a,b] ^{1}H NMR titration of **L1** in D_2O revealed an upper-field shift of anthracene resonances at pH >9 (Figure S5[11]), implying the presence of the π-stacking interaction of the two fluorophores within the **L1** species.

At pH <9, **L1** shows a characteristic absorption band (ca. 300−400 nm) attributable to the anthracene fragment (Figure 3A). However, at pH >9, the red-shifted absorption band

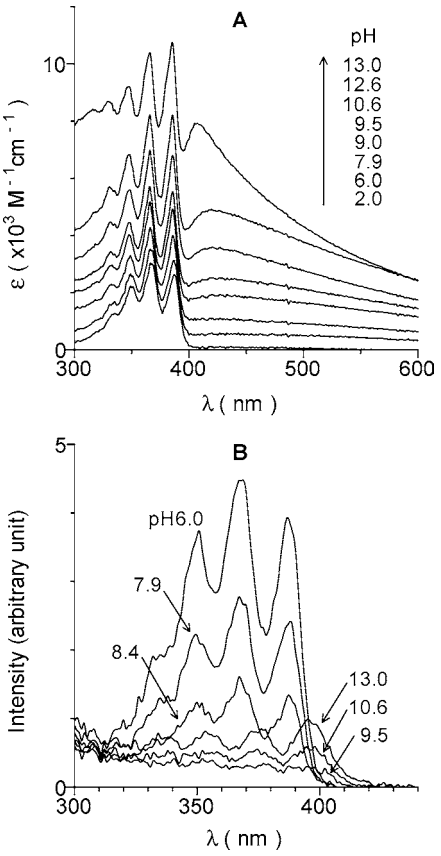

Figure 3. (A) Absorption and (B) excitation (λ_{em} = 520 nm) spectra of **L1** in aqueous NaCl (0.15 M) solution at 298 K.

appears (400−500 nm). This absorbance increases with a pH increase, which is consistent with increases in the quantity of the **L1** species and the intensity of the excimer emission (Figure 2B). The Beer's law plot [**L1** concentration in water (pH 13) vs absorbance of the red-shifted band at 402 nm] gives a straight line (Figure S1[11]). This indicates that the red-shifted absorption band is attributed not to an intermolecular aggregation of **L1** in solution but to the formation of an ICT-type complex in the ground state. Such red-shifted absorption does not appear in the case of **L4** (Figure S10[11]), thus excluding the formation of ICT complex between the unprotonated amine−anthracene in the ground state.[13]

Excitation spectra of **L1** (pH 2−13), collected at 416 nm of the monomer emission wavelength (Figure S2[11]), are similar to the absorption spectra obtained at pH <9 (Figure 3A). However, as shown in Figure 3B, the excitation spectra, collected at 520 nm of the excimer emission wavelength, show a red-shifted band (400−450 nm) at pH >9, whose appearance is coincident with the formation of the **L1** species (Figure 2B) and the appearance of the ICT absorption band (Figure 3A). Considering the present photoexcitation condition (λ_{ex} = 402 nm), the excimer emission may therefore be attributed to an excimer formed via a direct photoexcitation of the ground-state ICT complex, which is formed by the complete deprotonation of **L1** at basic pH (>9).

When acetonitrile, which has lower dielectric constant (ϵ = 38.8) than H_2O (ϵ = 78.5), is added to H_2O (pH 13), the excimer emission intensity of **L1** decreases with the quantity of acetonitrile: the addition of 10%, 13%, and 50% acetonitrile leads to a 10%, 50%, and 77% decrease in the emission intensity (Figure S3[11]). In these cases, the ICT absorption and excitation bands decrease in parallel. These findings indicate that the ground-state ICT complex of **L1** may be formed by a solvation of polar H_2O molecules. However, in D_2O (pH 13) of similar dielectric constant (ϵ = 78.1) to H_2O, a 48% decrease in the excimer emission intensity is observed, along with the decrease in the ICT absorption band (Figure S3[11]). This is because D_2O has a more ordered and stable structure than H_2O owing to stronger hydrogen bonding and the solvation of D_2O to **L1** is weaker than that of H_2O.[14] In H_2O (pH 13), the excimer emission intensity of **L1** decreases as the temperature rises, along with a decrease in the ICT absorption band (Figure S4[11]). This is because the H_2O solvation becomes weaker with a rise in temperature.[15] The above findings strongly suggest that the H_2O solvation to the fully unprotonated **L1** species triggers the ground-state ICT complex formation. As studied extensively,[16] 9,9′-bianthryl and polymethylene- and polyoxyethylene-bridged di(9-anthracenes) do not form a ICT complex in the ground state, but form in the excited state by solvation of polar solvent molecules leading to an excimer emission. This unexpectedly strong ground-state intramolecular association of **L1** may be caused by a combination of (i) pH-induced π-stacking interaction of the two fluorophores, (ii) the inherent electron donating property of the unprotonated amines, and (iii) strong solvation of H_2O molecules.

L2 and **L3** molecules (Figure 1),[17] comprised of longer polyamine chains than **L1**, also show excimer emission at

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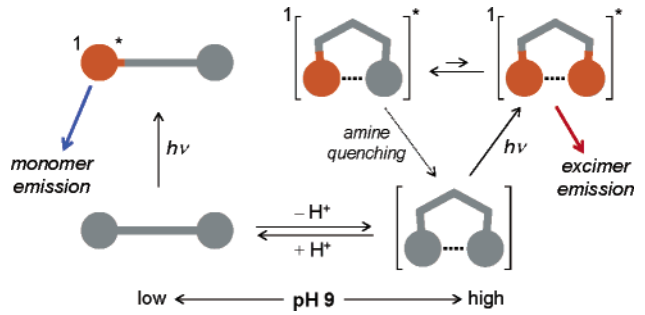

Figure 4. Mechanism of pH-controlled fluorescence switching of **L1** in water when excited at $\lambda_{ex} = 402$ nm.

basic pH, but the intensities of the spectra (excimer emission, ICT absorption, and excitation bands) are significantly lower than those for **L1** (Figures S8 and S9[11]). This indicates that **L1** may have a more suitable structure for the π-stacking interaction of the two fluorophores required for the ground-state ICT complex formation.

In the excited state, excimer species (^{1}E*) usually lie in equilibrium with locally excited monomer species (^{1}M*), thus showing both monomer and excimer emissions at once.[7a,b,18] However, for **L1**, 402 nm photoexcitation at pH >9 allows only excimer emission (Figure 2). In contrast, upon 368 nm excitation of **L1** where more ^{1}M* might be formed than 402 nm excitation, higher monomer emission intensity is observed (Figure S2[11]), as expected from the absorption specrum (Figure 3A), but the intensity of the excimer emission is negligibly small. This indicates that the excited-state equilibrium practically does not exist between ^{1}M* and ^{1}E* species for **L1**. This is also confirmed by nanosecond time-resolved fluorescence measurements ($\lambda_{ex} = 368$ and 400 nm) monitoring at 440 and 520 nm for respective monomer and excimer emissions (Figure S6 and Tables S2 and S3[11]). Upon 400 nm excitation at pH 13, where only the ICT complex exists, the fluorescence decay is explained by double-exponential with decay times of 0.01 and 2.47 ns. Based on their lifetime, the respective species can be ascribed to ^{1}M* and ^{1}E* species.[19] At both detection wavelengths (440 and 520 nm), ^{1}M* species give negative preexponential factors,[20] where almost all of the contribution (100%) is made by ^{1}E* species. However, upon 368 nm excitation, the preexponential factors for the respective species are estimated to be 98% and 2% (at 440 nm) and 78% and 22% (at 520 nm). At basic pH, ^{1}M* formed via ^{1}E* upon 402 nm excitation is strongly quenched by an electron transfer from the unprotonated amines, thus suppressing the monomer emission (Figure 4). Upon 368 nm excitation, ^{1}E* formation via ^{1}M* is suppressed by the rapid amine quenching of ^{1}M*, thus allowing only weak excimer emission (Figure S7[11]). These findings clearly explain the nonequilibrium excited state between ^{1}M* and ^{1}E* species of **L1** at basic pH and, at the same time, strongly support the proposed direct photoexcitation mechanism of the ground-state ICT complex for the excimer emission (Figure 4).

In conclusion, we have demonstrated that a simple-structured molecule, **L1**, behaves as a molecular switch with an unprecedented pH-controlled absolute switching function of dual-mode fluorescence. This behavior exhibits significant advantage in comparison with previously reported switches:[1−7] (i) detection of basic pH is simply done by monitoring the disappearance of the monomer emission and the intensity of the excimer emission, while other switches "turn off" the total emission in basic media and (ii) the excimer emission of **L1** is observed in total water of basic pH and is decreased by an addition of solvents of lower dielectric constant, while other excimers and exciplexes reported are only stable in water of acidic-neutral pH or nonpolar solvents. The results presented here might be useful in the design of new anthracene-based switching materials.

Acknowledgment. This work was supported by the Grant-in-Aids for Scientific Research (No. 15360430) and the Grant-in-Aids for Scientific Research on Priority Areas (417) "Fundamental Science and Technology of Photofunctional Interfaces" (No. 15033244) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

Supporting Information Available: Chemical and photophysical properties and spectra of **L1**−**L4** (Figures S1−S10 and Tables S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The lifetime of the excimer emission of **L1** (2.47 ns) is significantly shorter than that of the reported excimer emissions of aromatic hydrocarbons (>10 ns). This is because, at the present basic condition (pH 13), the excimer (^{1}E* species) of **L1** is strongly quenched by an electron transfer from the unprotonated amines.

(20) The negative preexponential factors for the ^{1}M* species are because of rather shorter lifetime of the ^{1}M* species than that of the ^{1}E* species.