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pH- and H_2O-Driven Triple-Mode Pyrene Fluorescence

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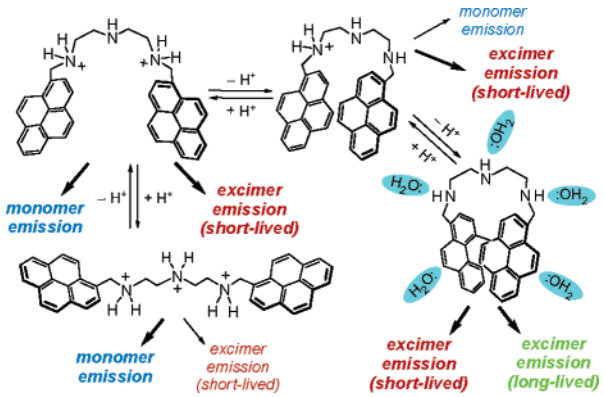
ABSTRACT



A simple-structured molecule L1, a diethylenetriamine bearing two end pyrene fragments, demonstrates triple-mode fluorescence consisting of monomer and short- and long-lived excimer emissions in water, which are precisely controlled by pH and an addition of a less-polar organic solvent.

The design and synthesis of fluorescent molecules whose emission properties can be modulated by external inputs is an area of intense research activity and of tremendous significance to the field of sensor device fabrication.[1] Pyrene-containing molecular systems have been studied extensively[2] because they demonstrate distinctive monomer and excimer emissions. Various pyrene systems capable of switching the monomer/excimer emissions by external inputs (temperature, ions, and pH) in organic[3] or aqueous media[4] have been proposed so far; however, most of these systems show single-excimer emission. Three recent reports[5] have proposed more integrated pyrene systems capable of switching the monomer and multiple-mode excimer emissions, but they act only in organic media.

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Our pyrene system presented here is the first example capable of switching the monomer and dual-mode excimer emissions in water. This system is based on a simple-structured molecule **L1**, a diethylenetriamine bearing two pyrene fragments at the respective ends (Figure 1). The triple-

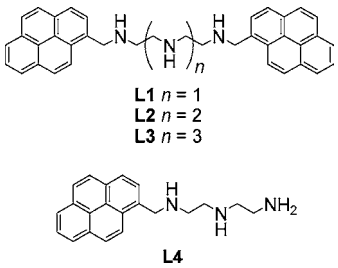

Figure 1. Structure of polyamines bearing end pyrene fragments, **L1**−**L4**.

mode emissions are precisely controlled by pH and an addition of a less-polar organic solvent. The monomer emission appears at acidic−neutral pH. The excimer emissions consisting of short- and long-lifetime species appear at basic pH, where the latter long-lifetime emission is weakened by the addition of an organic solvent. We describe here that this unprecedented emission switching function of **L1** in water is promoted by a pH-controlled bending movement of the polyamine chain leading to a formation of an intramolecular ground-state dimer (GSD) of the pyrene fragments and by solvation of the dimer by H_2O molecules.

The **L1** molecule is easily synthesized by reaction of diethylenetriamine with pyrene-1-carbaldehyde in ethanol, followed by reduction with $NaBH_4$.[6] As shown in Figure 2A, **L1** dissolved in water with acidic−neutral pH shows a distinctive fluorescence at 370−420 nm (λ_{ex} = 360 nm), which is attributable to a monomer emission from the locally excited pyrene fragment. As observed for related pyrene-conjugated polyamines,[7] the intensity of this monomer emission decreases with deprotonation of the nitrogen atoms

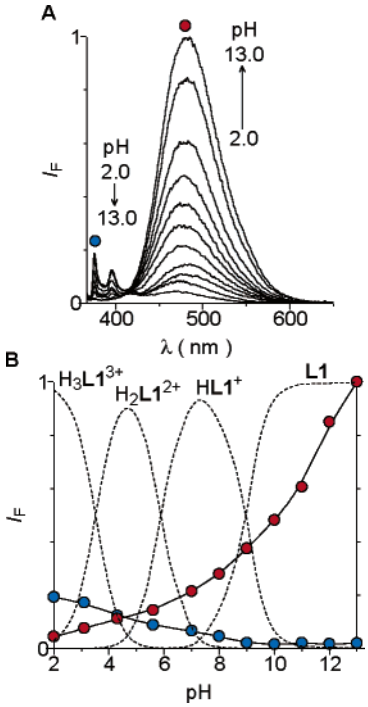

Figure 2. (A) Change in fluorescence spectra (λ_{ex} = 360 nm) of **L1** (25 μM) with pH in aqueous NaCl (0.15 M) solution at 298 K. (B) Mole fraction distribution of the different **L1** species (dotted line) and intensity of the emissions monitored at (blue) 376 nm and (red) 480 nm.

of **L1**. This is because the unprotonated amines are efficient electron-transfer quenchers of the excited pyrene.[1d] This trend is illustrated in Figure 2B, where the emission intensity monitored at 376 nm is plotted against pH (blue symbol) together with the mole fraction distribution of the different **L1** species (dotted line), which is calculated from the protonation constants determined potentiometrically.[8] The fully protonated form of **L1** (H_3**L1**$^{3+}$ species) exhibits the most intense emission, whereas total emission quenching occurs upon removal of a proton from the H**L1**$^{+}$ species.

A notable feature of the fluorescence spectra of **L1** (Figure 2A) is the presence of a red-shifted emission band at 420−600 nm, which is observed at the entire pH range. **L4** containing a single pyrene unit (Figure 1)[9] does not show such a red-shifted emission (Figure S3[10]). This implies that the red-shifted emission of **L1** is due to an intramolecular excimer formed via an association of two end pyrene fragments within the molecule. The intensity of this excimer emission monitored at 480 nm increases with a pH increase (Figure 2B, red symbol). This can be ascribed to a decrease in the electrostatic repulsion of the polyamine chain associated with the deprotonation of the nitrogen atoms,[11] which

(6) 1,7-Bis(1-methylpyrenyl)-1,4,7-triazaheptane (**L1**). This material was synthesized in a manner similar to the syntheses of **L2** and **L3**,[7] as follows: pyrene-1-carbaldehyde (0.46 g, 2.0 mmol), diethylenetriamine (0.10 g, 1.0 mmol), and an activated NaX zeolite molecular sieve (4 g) were refluxed in CH_2Cl_2 (100 mL) with magnetic stirring for 2 h under dry N_2. The solution was recovered by filtration and concentrated by evaporation. The resulting oil was dissolved in ethanol (100 mL) and stirred with $NaBH_4$ (0.22 g, 6.0 mmol) at 333 K for 2 h and at room temperature for 16 h. The resultant was concentrated by evaporation, dissolved in CH_2Cl_2, washed with an aqueous NaOH solution (1 mol/L, 25 mL × 3), and concentrated by evaporation. The semisolid residue was dissolved in ethanol and precipitated by addition of an aqueous HCl (35%) solution as its HCl salt, which was washed with CH_2Cl_2 and dried in vacuo (orange powder, 0.31 g, yield 48%). ^{1}H NMR (270 MHz, d_6-DMSO, TMS): δ (ppm) = 3.50−3.60 (m, 4H, CH_2 of diethylenetriamine), 5.04 (s, 4H, ArCH_2), 8.12−8.62 (m, 18H, Ar*H*). ^{13}C NMR (270 MHz, d_6-DMSO, TMS): δ (ppm) = 42.8, 43.0, 47.2, 123.0, 123.3, 123.6, 124.5, 125.0, 125.4, 125.6, 126.3, 126.9, 127.9, 128.7, 128.9, 129.9, 130.4, 131.2. FAB MS spectrum, *m/e* 532.2 (M+). Anal. Calcd for $C_{38}H_{33}N_3$·3HCl: C, 71.19; H, 5.66; N, 6.55. Found: C, 71.82; H, 5.60; N, 6.43. ^{1}H NMR, ^{13}C NMR, and FAB MS spectra for **L1**: see Figures S8−S10.[10]

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(8) 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 for **L1**: log *K*(H**L1**/H·**L1**) = 8.97, (H_2**L1**/H**L1**·H) = 6.02, and (H_3**L1**/H_2**L1**·H) = 3.48. For the protonation constants for the other materials: see Table S1.[10]

allows the required bending movement of the polyamine chain for the association of end pyrene fragments.

L4 shows a distinctive absorption band attributable to a pyrene unit (λ_{max} = 342 nm; Figure S3[10]). In contrast, **L1** shows a red-shifted absorption band (λ_{max} = ca. 365 nm) at the entire pH region (Figure 3A).[12] This implies the formation

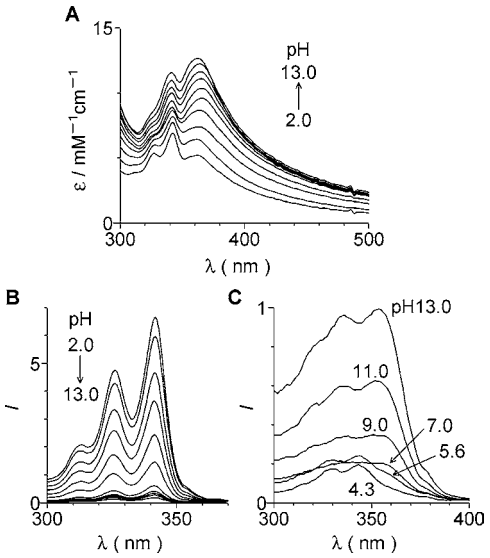

Figure 3. pH-dependent change in (A) absorption and excitation spectra collected at (B) 376 nm and (C) 480 nm of **L1** in aqueous NaCl (0.15 M) solution at 298 K.

of an intramolecular ground-state dimer (GSD) of the end pyrene fragments within **L1**.[13] The absorbance of this red-shifted band increases with a pH increase, indicating that the GSD is more stabilized by the pH-induced bending of the polyamine chain. As shown in Figure 3B, excitation spectra of **L1** collected at 376 nm (monomer emission) are similar to the excitation and absorption spectra of **L4** (λ_{max} = 342 nm; Figure S3[10]). In contrast, excitation spectra of **L1** collected at 480 nm (excimer emission) show a red-shifted band (Figure 3C), which is consistent with the red-shifted GSD absorption (Figure 3A). These findings clearly indicate that the excimer emission of **L1** is due to an excimer formed via a direct photoexcitation of the GSD. This is confirmed by the dependence of the excimer/monomer emission intensity ratio of **L1** on the excitation wavelength:[14] a significant increase in the ratio is observed at excitation wavelengths of >350 nm (Figure S5[10]). This fact strongly supports the direct GSD photoexcitation mechanism for the excimer formation. Nanosecond time-resolved emission decay measurements of **L1** at 480 nm reveal that the lifetime of the excimer emission increases with the deprotonation of **L1** (Table S2[10]): H_3**L1**$^{3+}$ (4.0 ns) < H_2**L1**$^{2+}$ (4.6 ns) < H**L1**$^{+}$ (5.3 ns). This indicates that the GSD stabilization, associated with the pH-induced bending of the polyamine chain, leads to the formation of a more stable excimer.[15]

It is notable that the **L2** and **L3** molecules (Figure 1),[7] comprised of longer polyamine chains than **L1**, show neither excimer emission nor red-shifted GSD absorption at the entire pH range (Figures S1 and S2[10]). This suggests that the length and bending angle of the diethylenetriamine ligand and the resulting configuration of the end pyrene fragments within **L1** are crucial for GSD formation.

At pH > 8, the excimer emission intensity of **L1** is quite strong, whereas the monomer emission intensity is almost zero (Figure 2B). These occur in conjunction with a formation of the fully deprotonated **L1** species, implying that GSD is highly stabilized via the complete polyamine deprotonation. The most notable feature of the excimer emission of the fully deprotonated **L1** species is that *this emission involves two emitting species*. The decay of the excimer emission monitored at 480 nm (pH 13; Figure 4, closed circle symbol) is simply explained by the sum of two exponentials with lifetimes (preexponential factors) of 6.3 (77%) and 30.8 ns (23%) (Table S2[10]). The former species have a 1 ns longer lifetime than the excimer H**L1**$^{+}$ species (5.3 ns); this can be explained because the fully deprotonated **L1** species form a more stable GSD than the H**L1**$^{+}$ species (Figure 3A). However, the lifetime of the latter excimer species is unexpectedly long.

The appearance of the long-lifetime excimer emission at basic pH is ascribed to a stabilization of the GSD by H_2O solvation. When acetonitrile, of lower dielectric constant (ϵ = 38.8) than H_2O (ϵ = 78.5), is added to a solution (pH 13), the excimer emission intensity decreases with an increase in the acetonitrile quantity (Figure S6[10]), where the red-shifted GSD absorption decreases in parallel. This indicates that the GSD is destabilized by the addition of less-polar acetonitrile. However, in D_2O (pH 13) of dielectric constant (ϵ = 78.1) similar to H_2O, a 48% decrease in the excimer

(9) 1-(1-Methylpyrenyl)-1,4,7-triazaheptane (**L4**). This material was synthesized in a manner similar to the synthesis of **L1**,[6] with pyrene-1-carbaldehyde (0.23 g, 1.0 mmol), diethylenetriamine (1.0 g, 10 mmol), and $NaBH_4$ (0.11 g, 3.0 mmol), affording an orange powder (as HCl salt, 0.58 g, yield 67%). ^{1}H NMR (270 MHz, d_6-DMSO, TMS): δ (ppm) = 3.50−3.60 (m, 4H, CH_2 of diethylenetriamine), 5.03 (s, 2H, ArCH_2), 8.11−8.62 (m, 9H, Ar*H*). ^{13}C NMR (270 MHz, d_6-DMSO, TMS): δ (ppm) = 35.1, 42.7, 43.1, 43.9, 47.3, 123.1, 123.4, 123.7, 124.6, 125.1, 125.4, 125.6, 126.4, 127.0, 128.0, 128.8, 129.0, 130.0, 130.5, 131.2. FAB MS, *m/e* 318.1 (M+). Anal. Calcd for $C_{21}H_{23}N_3$·3HCl: C, 59.10; H, 6.14; N, 9.85. Found: C, 59.45; H, 6.26; N, 9.77. ^{1}H NMR, ^{13}C NMR, and FAB MS spectra for **L4**: see Figures S11−S13.[10]

(10) See Supporting Information.

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(12) The Beer's Law plot [**L1** concentration in water against the absorbance of this red-shifted band] gives a straight line (Figure S4[10]). In addition, filtration of the **L1** solution does not lead to a decrease in the intensities of excimer emission and the absorption band. These findings exclude the possibility of an intermolecular aggregation of **L1** in solution.

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(15) In contrast, the lifetime of the monomer emission decreases with the deprotonation of **L1**: H_3**L1**$^{3+}$ (121 ns) > H_2**L1**$^{2+}$ (97 ns) > H**L1**$^{+}$ (79 ns) (see Table S2[10]). This is because the deprotonation of polyamine accelerates the electron transfer from the unprotonated amines to the pyrene unit.[1d]

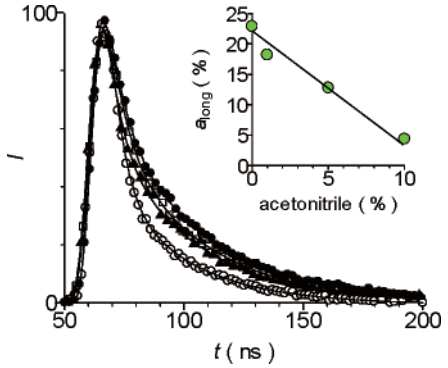

Figure 4. Excimer emission decays (λ_{ex} = 358 nm; λ_{em} = 480 nm; 298 K) of **L1** in aqueous NaCl (0.15 M) solution (pH 13) with different acetonitrile content (closed circle, 0%; open square, 1%; closed triangle, 5%; open circle, 10%). (Inset) Change in the preexponential factor of the long lifetime emission (a_{long}) with the acetonitrile content. For detailed time-resolved data, see Table S3.[10]

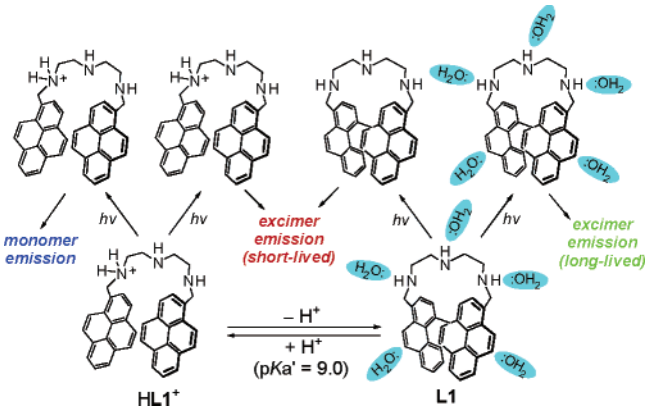

Figure 5. Schematic representation of the mechanism for pH- and H_2O-driven triple-mode pyrene fluorescence of **L1** in water.

emission intensity is still observed, along with the GSD absorption decrease (Figure S6[10]). This is because D_2O has a more ordered and stable structure than H_2O owing to a stronger hydrogen bonding, resulting in a weaker solvation to **L1** than H_2O.[16] These findings clearly indicate that H_2O solvation stabilizes the GSD of the fully deprotonated **L1** species; hence, the long-lifetime excimer emission is attributable to a highly stabilized excimer formed by direct photoexcitation of the H_2O-solvated GSD (Figure 5).[17]

Another notable feature of the excimer emission of **L1** at basic pH is that *the long-lifetime emission is controlled by the quantity of less-polar organic solvent added*. As shown in Figure 4 (inset), the preexponential factor of the long-lifetime species (a_{long}) decreases linearly with an increase in the acetonitrile content, along with the GSD absorption decrease (Figure S6[10]). This suggests that the stability of the H_2O-solvated GSD is responsive to the less-polar solvent quantity in water, thus allowing the precise control of the long-lifetime emission. In general, excimers and exciplexes are more stable in less-polar media.[18] The long-lifetime excimer formed in the **L1** system is the first example showing the highest stability in highly polar aqueous media.

In summary, we have found that a simple-structured molecule, **L1**, demonstrates triple-mode fluorescence driven by pH and H_2O. The basic concept presented here for controlling the multiple-mode pyrene fluorescence in water by a simple polyamine ligand and by simple chemical inputs may contribute to the development of more integrated fluorescent molecular systems based on a pyrene fluorophore.

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Supporting Information Available: Instruments and measurements, Tables S1−S4, and Figures S1−S13. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The formation of the H_2O-solvated GSD is also confirmed by the facts that the preexponential factor of the long lifetime species and the GSD absorption decrease as the temperature rises (Table S4 and Figure S7).[10] This is because the H_2O solvation becomes weaker with a rise in temperature: Szabo, M. I. A.; Goring, D. A. I. *J. Chem. Soc. A* **1968**, 1500−1503.

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