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9-(Cycloheptatrienylidene)-fluorene Derivative: Remarkable Ratiometric pH Sensor and Computing Switch with NOR Logic Gate

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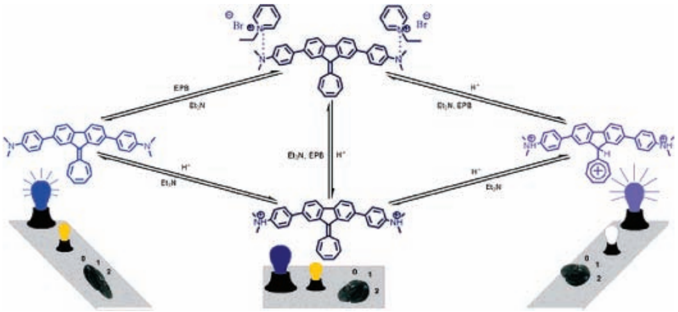
ABSTRACT



2,7-Bis(4-dimethylaminophenyl)-9-(cycloheptatrienylidene)fluorene (1) was synthesized and characterized. 1 could be used as a fluorescent sensor either for pH or for pyridinium halide. Integrated with the ratiometric method and an NOR logic gate, a tunable two-input/multi-output system was presented on the basis of this single molecule.

Sensors have been developed to construct molecular machines such as shuttles,[1a] rotors,[1b] muscles,[1c] ratchets,[1d] pistons and cylinders,[1e] scissors,[1f] and elevators.[1g] Compared to absorbent sensors, fluorescent sensors and probes with high sensitivities have been applied in a variety of areas such as industry, environment, and medicine.[2] In particular, a fluorescent signal can be detected in a single molecule.[2b,c,3] Recently, multifunctional fluorophore systems,[4] and so-called AND/OR logic gates,[5] raised new prospects in combined sensing applications. Several logic functions integrated within a single molecule have been used, not only for recognizing the chemical inputs, but also for light signals.[6] On the basis of functional integration, the half-adder[7] and half-subtractor[8] based on a single molecule was constructed to build a full adder in order to accelerate the calculation and to increase

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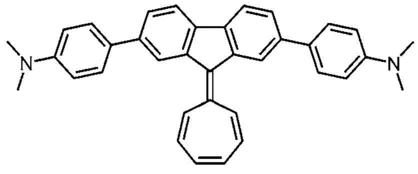
computer storage. However, most of them were based on multi-input/two-output functions with few showing multi-output functions.[9] It is likely that the conventional interactive computing system, which consists of two channels of input (keyboard and mouse) and two channels of output (monitor and speaker) forming a canonical interactive loop, is no longer suitable due to the growing demands of human users. As a result, interactive media design has been focused on the creation of nouveau pop-up books to present a highly simplified set of one-input/three-output (visual, aural, and tactile) interactive systems.

Meanwhile, it has been proposed that molecular logic gates could be powered by superior processing capabilities, which are based on a two-input/multi-output system. Each chemical input can be recognized within a single molecule, forming ideally distinct chemical states with corresponding characteristic signals. These different outputs can be displayed by multiple media systems simultaneously, such as monitor, speaker, printer, projection, etc. This approach has been used to design functional molecules and their applications in molecular devices.

In principle, molecule construction with photoinduced electron transfer (PET)[10] or charge transfer (PCT)[11] between fluorophore and receptor systems is one of the most frequently used pathways for building useful sensors and molecular machines.[2b,12] When its receptor is combined with the analytes, the molecule can display “on−off”, “off−on”, “on−off−on”,[13] or “off−on−off”[14] fluorescence emissions upon various analytes. Aromatic amines are typical examples[15,16] of pH fluorescent sensors because their fluorescent spectra can be changed reversibly by protonation/deprotonation. Meanwhile, it is a challenge to design molecules with dual emission properties as the remarkable advantages of the ratiometric method.[2b,c]

In our previous reports, 9-(cycloheptatrienylidene)-fluorene (9-CHF)[17a] served as an efficient absorbent sensor, which can be applied in acidic conditions (1.5 to 3.5 mol L^{-1} H_2SO_4 in ethanol). 2,7-Diaryl-9-(cycloheptatrienylidene)fluorenes (DA-9-CHFs),[17b] despite their use as efficient absorbent sensors, could be used as fluorescent sensors under mildly acidic conditions (0.05 to 1.20 mol L^{-1} H_2SO_4 in THF). In this paper, a new fluorene derivative, 2,7-bis(4-dimethylaminophenyl)-9-(cycloheptatrienylidene)fluorene (**1**) was synthesized as previously reported[17b] in 52% yield. This compound, integrating PET and PCT, demonstrated potential applications in molecular devices. The maximum absorption wavelength of **1** was 370 nm with a shoulder at 420 nm. Excited at 321 nm under neutral conditions, **1** exhibited a maximum emission wavelength of 409 nm. When the pH value was decreased to 3.45, the absorbent band was blue-shifted to 330 nm with a slight increase in absorbance. However, a further decrease in pH led to a distinct increase in the absorbance at 330 nm, and the shoulder at 420 nm completely disappeared. The isobestic point of the adsorption curves was at 380 nm. The solution color changed from orange to colorless. Meanwhile, it was noted that the PL quantum yield[18] decreased as the pH value dropped from 7.06 to 4.00 ($\Phi_F = 0.40$ to 0.097%). When the pH value was decreased further to 0.97, the PL quantum yield increased remarkably ($\Phi_F = 0.097$ to 2.6 %). A fluorescent sensor with “on−off−on” behavior was observed in the pH range of 7.06−0.97 (Figure 1).

Scheme 1. Structure of **1**



1

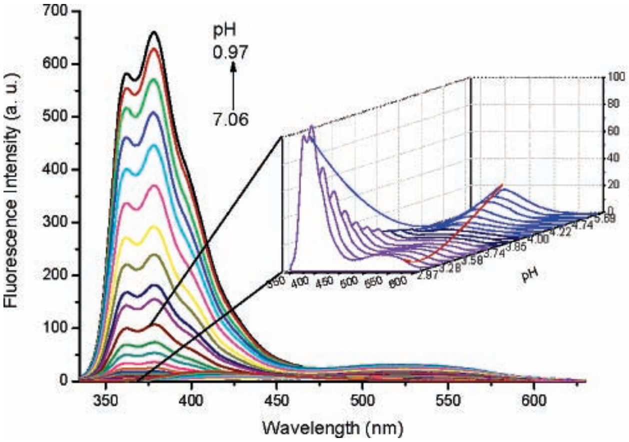


Figure 1. pH dependence of the PL spectra of **1** (2.5 μM) as a function of pH in water/ethanol (1:1, v/v) in the presence of 0.1 M KCl.

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The calculated ratios of emission intensities and absorbance are shown in Figure 2. It was interesting that the emission ratios (relative intensity at 350 vs 420 nm) varied in the pH range of 4.5−3.0; the absorbance ratios (absorptions at 325 vs 425 nm) changed in the pH range of 3.25−1.0. In a wider range of pH (4.5−1.0), it was noted that the ratios of emission (relative intensity at 350 vs 518 nm) increased with decreases in pH in an almost linear fashion (Figure 2). As a result, **1** could be applied as an efficient sensor with the ratiometric method in a broad pH range from 4.5 to 1.0.

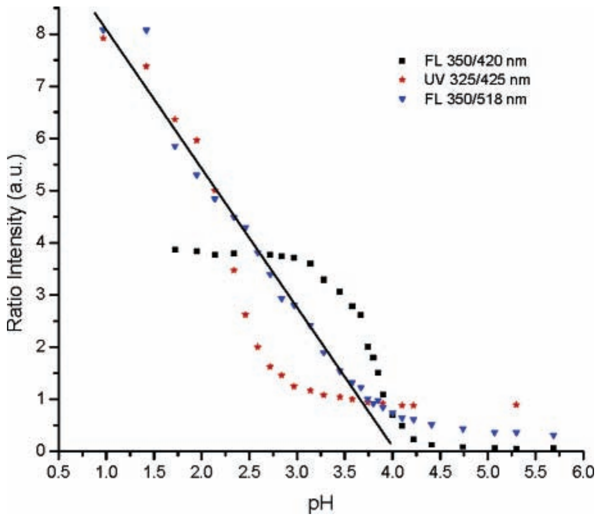

Figure 2. Ratios of the absorbance and ratios of the emission as a function of pH.

The mechanism of fluorescence “on−off−on” behavior was postulated in Scheme S1 (Supporting Information). At the very beginning, **1** had locally excited (LE) emission at 409 nm under neutral conditions. After protonation of DMA groups, the emission was switched off. The reason might be that protonation of DMA groups, which changes DMA from an electron donor into an electron acceptor, enhanced the PET process from a seven-member ring to a five-member ring.[19] As the solution was acidified, a sudden change in the absorption spectra occurred at pH 3.0; nevertheless, a remarkable change in emission spectra (the two new bands at 375 and 520 nm) was noted around pH 4.0. This means that the excited state of $\mathbf{1{+}2H^{2+}}$ was protonated more easily than the ground state. This mechanism[20] was well-known, namely, that the excited state was more strongly destabilized by protonation than the ground state when the proton interacted with the donor group, resulting in a blue-shift of the absorption and emission spectra. The dual emission was observed at a pH value lower than 4.0; 375 nm emission can be attributed to the locally excited emission of $\mathbf{1{+}3H^{3+}}$. Emission at 520 nm might be from fully charge-separated exciplex to $\mathbf{1{+}2H^{2+}}$. The linear behavior of emission ratios (relative intensities at 350 vs 518 nm, Figure 2) supports this proposal. According to the literature,[10] pK_a values (pK_a ($\mathbf{1{+}H^{+}}$), pK_a ($\mathbf{1{+}2H^{2+}}$), and pK_a ($\mathbf{1{+}3H^{3+}}$) were 5.0 ± 0.1, 3.5 ± 0.1, and 2.2 ± 0.1, respectively) were calculated to indicate these protonation stages. Different electron densities of the strongest excited states of **1**, $\mathbf{1{+}H^{+}}$, $\mathbf{1{+}2H^{2+}}$, and $\mathbf{1{+}3H^{3+}}$ were calculated by using AM1 parametrization in the WinMOPAC V2.0 program. The postulated enhancement of the PET process induced by PCT could be well explained by the changes of electron densities.

N-Alkylpyridinium cations should also enhance the PET process due to the charge-transfer interaction[21] between *N*-ethylpyridinium and DMA groups. When a certain amount of *N*-ethylpyridinium bromide (EPB) in water/ethanol (1:1, v/v) was added to the dilute solution of **1**, fluorescence was switched off. Use of triethylamine, a stronger electron-donating compound, suppressed the charge-transfer interaction. Thus, **1** was released and fluorescence was switched on. The solution color remained orange through this reversible process. However, when the solution was acidified instead of adding triethylamine, *N*-ethylpyridinium cation would be replaced by proton, resulting in the formation of $\mathbf{1{+}2H^{2+}}$ and $\mathbf{1{+}3H^{3+}}$. Fluorescence was switched on, and the solution faded to colorless. Therefore, **1** might be further utilized as a sensor for both proton and pyridinium cations (Figure S3, Supporting Information).

In the present context, either addition of a certain amount of EPB or acidifying the solution to pH = 4.1 ± 0.3 led to an apparent decrease in emission intensity at 409 nm (O_1 state “0”, $\Phi_F < 0.2\%$), which could be reversed by adding Et_3N (O_1 state “1”, $\Phi_F > 0.2\%$). The decreasing PL efficiency either by binding proton or EPB resulted in the possibility of **1** as an NOR logic gate. As shown in Figure 3, if the pH value was decreased further to <3.8 (I_2 state “2”, pH ≤ 3.8), a strong and tunable fluorescence signal was observed (O_1 state “1”, $\Phi_F > 0.2\%$) due to the formation of $\mathbf{1{+}3H^{3+}}$. A rheostat based on detectable emission intensity relying on variable pH was established. The state “1” of O_1 had two concepts: dual emissions (375 and 520 nm) and high PL efficiency ($\Phi_F \geq 0.4\%$). Meanwhile, the absorbance at 330 nm increased, and that at 420 nm decreased. This resulted in a change in the color of the solution from orange (O_2 state “0”, color) to colorless (O_2 state “1”, colorless). Thus, a special two-output switchable system with an NOR logic gate integrated within a single molecule was approached.

As mentioned above, a tunable switch system, using emission and absorption as output signals, was established. However, it will be more valuable if the ratiometric technique

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(18) Quantum yields were calculated using *trans*,*trans*-1,4-diphenylbuta-1,3-diene as the standard ($\Phi_F = 0.44$): Allen, M. T.; Miola, L.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 3198.

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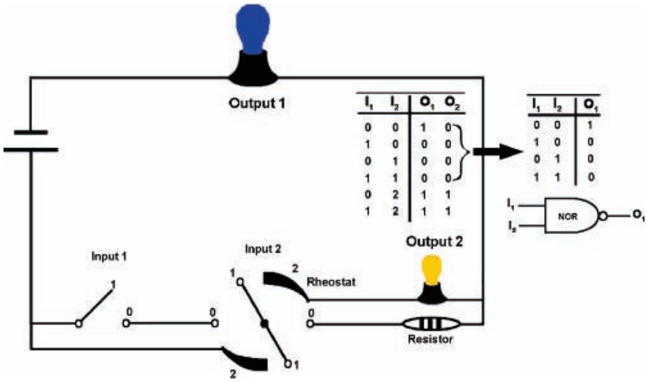

I_1	I_2	O_1	O_2
0	0	1	0
1	0	0	0
0	1	0	0
1	1	0	0
0	2	1	1
1	2	1	1

I_1	I_2	O_1
0	0	1
1	0	0
0	1	0
1	1	0

Figure 3. Illustration of the working mode of a tunable switch-integrated NOR logic system under the action of two inputs along with their representation based on electric circuit schemes (I_1: state "0", EPB = 0 mM; state "1", EPB ≥ 1.72 mM. I_2: state "0", pH ≥ 4.4; state "1", pH = 4.1 ± 0.3; state "2", pH ≤ 3.8. O_1: state "0" Φ_F <0.2%; state "1", Φ_F > 0.2%. O_2: state "0", color; state "1", colorless).

can be combined with the above system, because the ratiometric technique has no relationship with the fluorophore concentration. Therefore, the ratios can be used as an additional output signal, and this system is illustrated in Figure 4. *Input 2* (I_2) represents acidity. The working range of channel B is the complement of that of channel A. This means that these two channels would be alternative. Output signal (O_A) was the simplified NOR logic gate when the channel A was selected for I_2. When the channel B was selected, not only the absorbance and emission intensity but also ratios of their intensities could be used as output signals. Output states, O_{B1}, O_{B2}, O_{B3}, and O_{B4} represented the absorbance at 420 nm (A_{420}), the ratio of absorbance (A_{325}/A_{425}), the emission intensity at 520 nm (I_{520}), and the ratio of emission intensity (I_{350}/I_{420}), respectively. Each one had its characteristic signal threshold. If their half values[22] acted as the decision thresholds, the truth table for each output was available (Tables 1 and 2). Interestingly, when output O_{B1} signal was detected by measuring the absorption at 330 nm, an NOT logic gate was transformed into a YES logic gate as shown in Table 1.

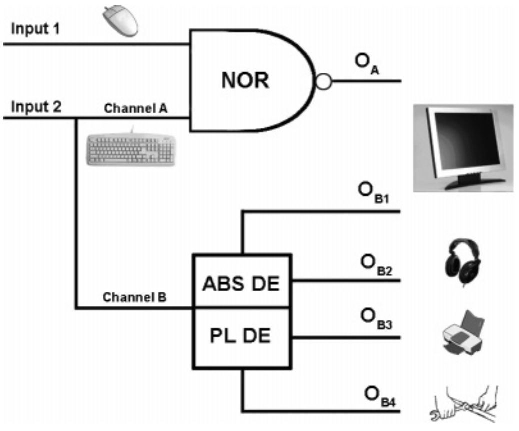

Figure 4. Illustration of two-input/multi-output system integrated NOR logic gate. ABS DE and PL DE are absorption and emission decision elements, respectively; O_{B1}, O_{B2}, O_{B3}, and O_{B4} are output states for absorption at 420 nm, the ratio of absorption, emission at 520 nm, and the ratio of emission intensity, respectively.

Table 1. Truth Table for ABS DE

I_1	O_{B1}	I_1	O_{B2}
0 (pH > 2.4)	1	0 (pH > 2.2)	0
1 (pH < 2.4)	0	1 (pH < 2.2)	1

Table 2. Truth Table for PL DE

I_1	O_{B3}	I_1	O_{B4}
0 (pH > 2.6)	0	0 (pH > 3.8)	0
1 (pH < 2.6)	1	1 (pH < 3.8)	1

In summary, several observations could be obtained. First, a new fluorene derivative, 2,7-bis(4-(dimethylamino)-phenyl)-9-(cycloheptatrienylidene)-fluorene (**1**), was synthesized and characterized. Second, **1** could be used as a fluorescent sensor not only for acidity but also for *N*-alkylpyridinium halide. Third, a controlled system with a two-input/multi-output function was established. The emission intensity, absorbance, ratios of emission intensities, ratios of absorbance, and solution color as detectable output signals could be integrated in a single molecule.

From 9-CHF[17a] as an absorption sensor applied in extremely high acid concentration, to DA-9-CHFs[17b] as both absorption and fluorescence sensors used for milder acidic environments, to **1** as a fluorescence sensor either for pH or for pyridinium cation, the applications of fulvene derivatives were well extended. With the addition of recognition elements such as pyridine or bipyridine motifs, crown ethers will lead to the derivatives with further different response capabilities. In other words, the present investigations demonstrate that the fulvene derivatives provide a pathway for fabrication of multifunctional instruments such as sensors, logic gates, and molecular devices.

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Supporting Information Available: Experimental details and characterization for new compounds reported.

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[22] Output decision value: state "0", $O < O_{min} + (O_{max} - O_{min})/2$; state "1", $O > O_{min} + (O_{max} - O_{min})/2$. O_{max} is the output value at the lowest pH value, and O_{min} is the output value at the highest pH value.