A fluorescent molecular logic gate with multiply-configurable dual outputs†

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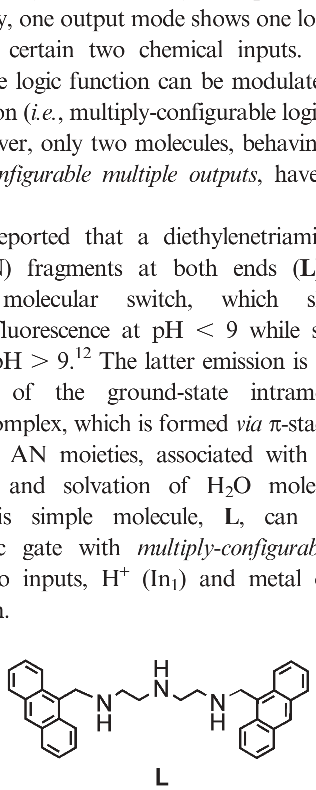
A simple molecule, L, diethylenetriamine bearing anthracene fragments at both ends, behaves as a fluorescent molecular logic gate with "multiply-configurable dual outputs", capable of demonstrating five different logic functions operated by proton (H^+) and transition metal cations (M^{n+}) as inputs.

Design and development of supramolecular systems, behaving as a molecular logic gate, is an area of intense research activity.[1] In particular, a system consisting of chemically encoded information as input and fluorescent signal as output has attracted a great deal of attention. Various molecular systems showing AND,[2] OR,[3] NOR,[4] INHIBIT,[5] XOR,[6] YES,[7] NOT,[8] and XNOR[9] functions have been proposed. Most of the molecules contain only one output mode (*i.e.*, single fluorescence). Recent interest is focused on an integrated system involving multiple fluorescent output modes.[1] Basically, one output mode shows one logic function by a combination of certain two chemical inputs. Construction of molecules, whose logic function can be modulated by a different input combination (*i.e.*, multiply-configurable logic), has now been a focus.[10] However, only two molecules, behaving as a logic gate with *multiply-configurable multiple outputs*, have been proposed until now.[11]

Earlier, we reported that a diethylenetriamine bearing two anthracene (AN) fragments at both ends (**L**) behaves as a pH-controlled molecular switch, which shows ordinary monomer AN fluorescence at pH < 9 while showing excimer fluorescence at pH > 9.[12] The latter emission is "on" by a direct photoexcitation of the ground-state intramolecular charge transfer (ICT) complex, which is formed *via* π-stacking interaction of the two end AN moieties, associated with the pH-induced chain bending, and solvation of H_2O molecules. Here we report that this simple molecule, **L**, can also act as a fluorescent logic gate with *multiply-configurable dual outputs* operated by two inputs, H^+ (In_1) and metal cations (In_2), in aqueous solution.



L

At pH 10 without H^+ and metal cations ($In_1(0)$–$In_2(0)$), **L** shows only excimer emission (Fig. 1).[12] The lack of monomer emission is attributable to an electron transfer (ET) from unprotonated nitrogen atom to the photoexcited AN;[13] hence, two outputs monitoring at 416 (Out_1) and 520 nm (Out_2) result in 0 and 1, respectively. Addition of H^+ to the solution (pH 8; 1–0) leads to a protonation of polyamine. This suppresses the ICT complex formation because of an electrostatic repulsion of the polyamine chain,[12] thus showing no excimer emission. On the other hand, the protonation of polyamine suppresses the ET from nitrogen atom to the photoexcited AN[12,13] and hence allows the monomer emission, resulting in 1 (Out_1) and 0 (Out_2) outputs.

With Zn^{2+} or Cd^{2+} at pH 10 (0–1), monomer emission appears (Fig. 1; Fig. S6, ESI†). This is because coordination of Zn^{2+} or Cd^{2+} with **L** leads to a decrease in electron density of nitrogen atom and hence suppresses the ET to the photoexcited AN.[13] In this condition, excimer emission also appears. As is also the case without metal,[12] red-shifted absorption and excitation spectra (λ_{em} = 520 nm), attributable to the ICT complex, are observed at pH > 10 (Fig. S1, ESI†). ^1H NMR analysis in D_2O (pH 12) with Zn^{2+} shows upper-field shift of AN resonances attributable to π-stacking interaction of two AN moieties (Fig. S9, ESI†). Addition of MeCN to H_2O (at pH 11) containing **L** and Zn^{2+} leads to a decrease in the excimer emission intensity, along with the decreases in the ICT absorption and excitation bands (Fig. S2, ESI†), as is also the case without metal.[12] The above findings suggest that, at basic pH, Zn^{2+}–**L** adduct still forms ICT complex *via* π-stacking interaction of two AN fragments and H_2O solvation, thus showing excimer emission *via* the direct excitation of the complex. At pH 8 with Zn^{2+} (1–1), monomer and only weak excimer emissions appear (Fig. 1). Mole fraction distribution, calculated from the stability constants determined potentiometrically (Table S1 and S2 and Fig. S1, ESI†), reveals that, at this pH, $\mathbf{L}Zn^{2+}$ species form mainly (85%), indicating that two end AN fragments are forced to stay close. However, ICT absorption and excitation bands do not appear (Fig. S1, ESI†). This may be because the positively-charged $\mathbf{L}Zn^{2+}$ species suppress the H_2O solvation. In contrast, at pH 10, coordination of two OH^- groups neutralizes the net charge of the complex ($\mathbf{L}Zn(OH)_2$ formation) (Fig. S1, ESI†), thus allowing ICT complex formation. The truth table (Fig. 1) shows that operation of **L** by H^+ and Zn^{2+} (or Cd^{2+}; Fig. S6, ESI†) expresses OR (Out_1) and NOT (Out_2) logic functions.

Operation by Hg^{2+} (as In_2) expresses different logic functions (Fig. 2): INH (Out_1) and NOT (Out_2). Addition of Hg^{2+} at pH 8 (1–1) leads to total emission quenching. The lack of monomer emission is because the coordinated Hg^{2+}, of high atomic number,

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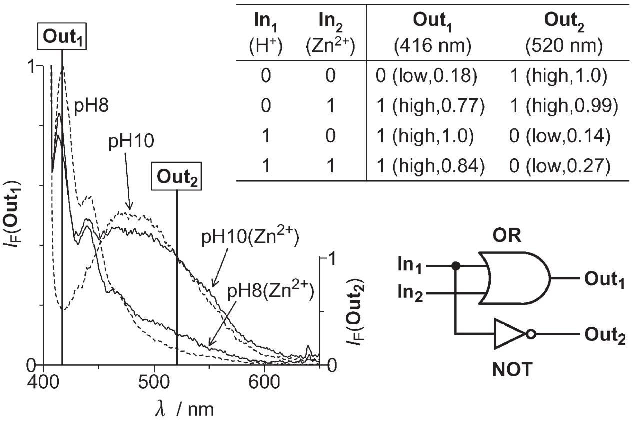
† Electronic supplementary information (ESI) available: properties and spectra of **L** in the presence of various metal cations (Table S1 and S2 and Fig. S1–S9). See http://dx.doi.org/10.1039/b510800d

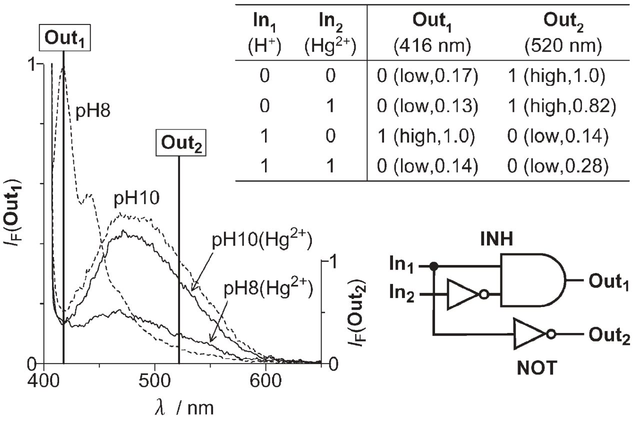


In$_1$ (H$^+$)	In$_2$ (Zn^{2+})	Out$_1$ (416 nm)	Out$_2$ (520 nm)
0	0	0 (low,0.18)	1 (high,1.0)
0	1	1 (high,0.77)	1 (high,0.99)
1	0	1 (high,1.0)	0 (low,0.14)
1	1	1 (high,0.84)	0 (low,0.27)

Fig. 1 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Zn^{2+} in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.

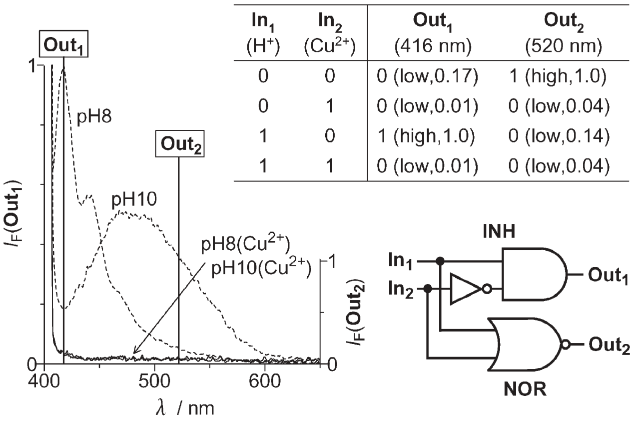
near the AN moieties enhances the intersystem crossing of the singlet excited-state AN to its triplet excited-state *via* a spin–orbital coupling (SOC).[14] At pH 10 with Hg^{2+} (0–1), monomer emission still does not appear, but excimer emission does appear. Absorption and excitation spectra obtained with Hg^{2+} (at pH > 9) are similar to those obtained with Zn^{2+} (Fig. S3, ESI†), and a similar upper-field shift of the AN resonances is observed (Fig. S9, ESI†). This indicates that ICT complex also forms in the presence of Hg^{2+}, thus allowing the excimer emission.

Operation by Cu^{2+}, Co^{2+} or Ni^{2+} (as In$_2$) leads to a complete quenching of the total emission both at pH 8 and 10 (Fig 3; Figs. S7 and S8, ESI†), expressing INH (Out$_1$) and NOR (Out$_2$) functions. The monomer emission quenching takes place because these coordinated ions lead to an *energy* transfer from the photoexcited AN to a low-lying empty d-orbital of the ions.[13,15] In this case, red-shifted absorption (Fig. S4, ESI†) and upper-field shift of the AN resonances (Fig. S9, ESI†) are observed at pH > 9, indicating that ICT complex forms even in the presence of these ions. The lack of the excimer emission at basic pH may therefore be because of the energy transfer from the excimer, formed by direct excitation of the ICT complex, to these adjacent d-metals.



In$_1$ (H$^+$)	In$_2$ (Hg^{2+})	Out$_1$ (416 nm)	Out$_2$ (520 nm)
0	0	0 (low,0.17)	1 (high,1.0)
0	1	0 (low,0.13)	1 (high,0.82)
1	0	1 (high,1.0)	0 (low,0.14)
1	1	0 (low,0.14)	0 (low,0.28)

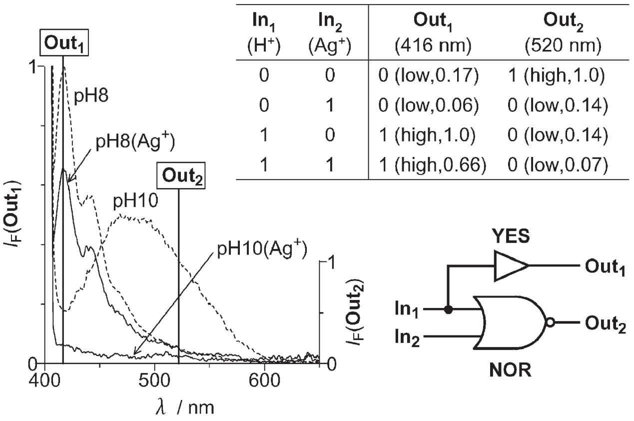
Fig. 2 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Hg^{2+} in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.



In$_1$ (H$^+$)	In$_2$ (Cu^{2+})	Out$_1$ (416 nm)	Out$_2$ (520 nm)
0	0	0 (low,0.17)	1 (high,1.0)
0	1	0 (low,0.01)	0 (low,0.04)
1	0	1 (high,1.0)	0 (low,0.14)
1	1	0 (low,0.01)	0 (low,0.04)

Fig. 3 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Cu^{2+} in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.

Operation by Ag^+ (as In$_2$) shows YES (Out$_1$) and NOR (Out$_2$) functions (Fig. 4). As well known, Ag^+ acts as the efficient quencher of the photoexcited monomer AN by the SOC effect, as does Hg^{2+}.[16] However, at pH 8 (1–1), monomer emission still appears. Comparison of the mole fraction distribution of the different **L** species with the change in the fluorescence intensity (Fig. S5, ESI†) indicates that complete quenching of the monomer emission occurs upon formation of **L**Ag^+ species. At pH 8, **L** still forms protonated species (H**L**Ag^{2+}; 65%). The monomer emission is, therefore, enhanced because of the ET suppression by the protonation of nitrogen atom.[13] At pH 10 (0–1), deprotonation of nitrogen atom takes place (formation of **L**Ag^+ and **L**Ag(OH) species) and hence quenches the monomer emission by the SOC effect. In this condition, excimer emission does not appear, although the presence of Hg^{2+} shows strong excimer emission (Fig. 2). ^{1}H NMR analysis demonstrates upper-field shift of the AN resonances in the presence of Ag^+ (Fig. S9, ESI†), but ICT absorption does not appear (Fig. S5, ESI†). In this case, absorbance at λ < 350 nm increases obviously by the coordination of Ag^+ with **L**. This absorbance increase is attributable to a formation of Ag^+–AN π complex.[17] These findings suggest that, at pH 10, Ag^+ situated near AN attracts π electron of AN moieties;



In$_1$ (H$^+$)	In$_2$ (Ag$^+$)	Out$_1$ (416 nm)	Out$_2$ (520 nm)
0	0	0 (low,0.17)	1 (high,1.0)
0	1	0 (low,0.06)	0 (low,0.14)
1	0	1 (high,1.0)	0 (low,0.14)
1	1	1 (high,0.66)	0 (low,0.07)

Fig. 4 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Ag^+ in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.

this suppresses the ICT complex formation, thus resulting in practically no excimer emission.

In conclusion, we have demonstrated that a simple-structured molecule, **L**, behaves as a fluorescent molecular logic gate with *multiply-configurable dual outputs*. This system is operated by H^+ and transition metal cations as inputs and is capable of demonstrating five different logic functions (OR, NOR, INHBIT, YES, NOT) by varying metal cation input. The concept presented here, which cleverly controls the monomer and excimer emissions by a simple molecule, may contribute to a construction of more miniaturized and integrated molecular level devices with multiple functions.

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