Supplementary Material for Chemical Communications

Supplementary data

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

Yasuhiro Shiraishi,* Yasufumi Tokitoh and Takayuki Hirai

A fluorescent molecular logic gate with multiply-configurable dual outputs

Yasuhiro Shiraishi,* Yasufumi Tokitoh, and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan. E-mail: shiraish@cheng.es.osaka-u.ac.jp

Electronic Supplementary Information (ESI†)

Table S1. Stepwise protonation constants of **L** determined in aqueous NaCl (0.15 M) solution at 298 K.[a]

Reaction[b]	
H + **L** ↔ H**L**	9.45 ± 0.06
H + H**L** ↔ H_2**L**	7.55 ± 0.16
H + H_2**L** ↔ H_3**L**	6.01 ± 0.30
Log β	23.01

[a] 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.
[b] Charges are omitted for clarity.

Table S2. Stability constants for interaction between **L** and metal cations (Zn^{2+}, Hg^{2+}, Cu^{2+}, and Ag^{+}) determined in aqueous NaCl (0.15 M) solution at 298 K.[a]

Reaction[b]	Zn^{2+}	Hg^{2+}	Cu^{2+}	Ag^{+}
M + **L** ↔ M**L**	8.92 ± 0.05	24.9 ± 0.12	17.6 ± 0.31	7.20 ± 0.17
M**L** + H ↔ MH**L**	6.97	4.3	3.81	8.39
M + **L**H ↔ MH**L**	6.84	20.1	12.4	6.54
M**L** + OH ↔ M**L**(OH)	4.41	8.00	10.0	4.84
M**L**(OH) + OH ↔ M**L**$(OH)_2$	4.80	6.38	9.59	–
M**L**$(OH)_2$ + OH ↔ M**L**$(OH)_3$	–	–	4.74	–
M + **L** + H_2O ↔ M**L**(OH) + H	–0.47 ± 0.24	19.1 ± 0.15	13.8 ± 0.27	–1.76 ± 0.13

[a] 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 stability constants.
[b] Charges are omitted for clarity.

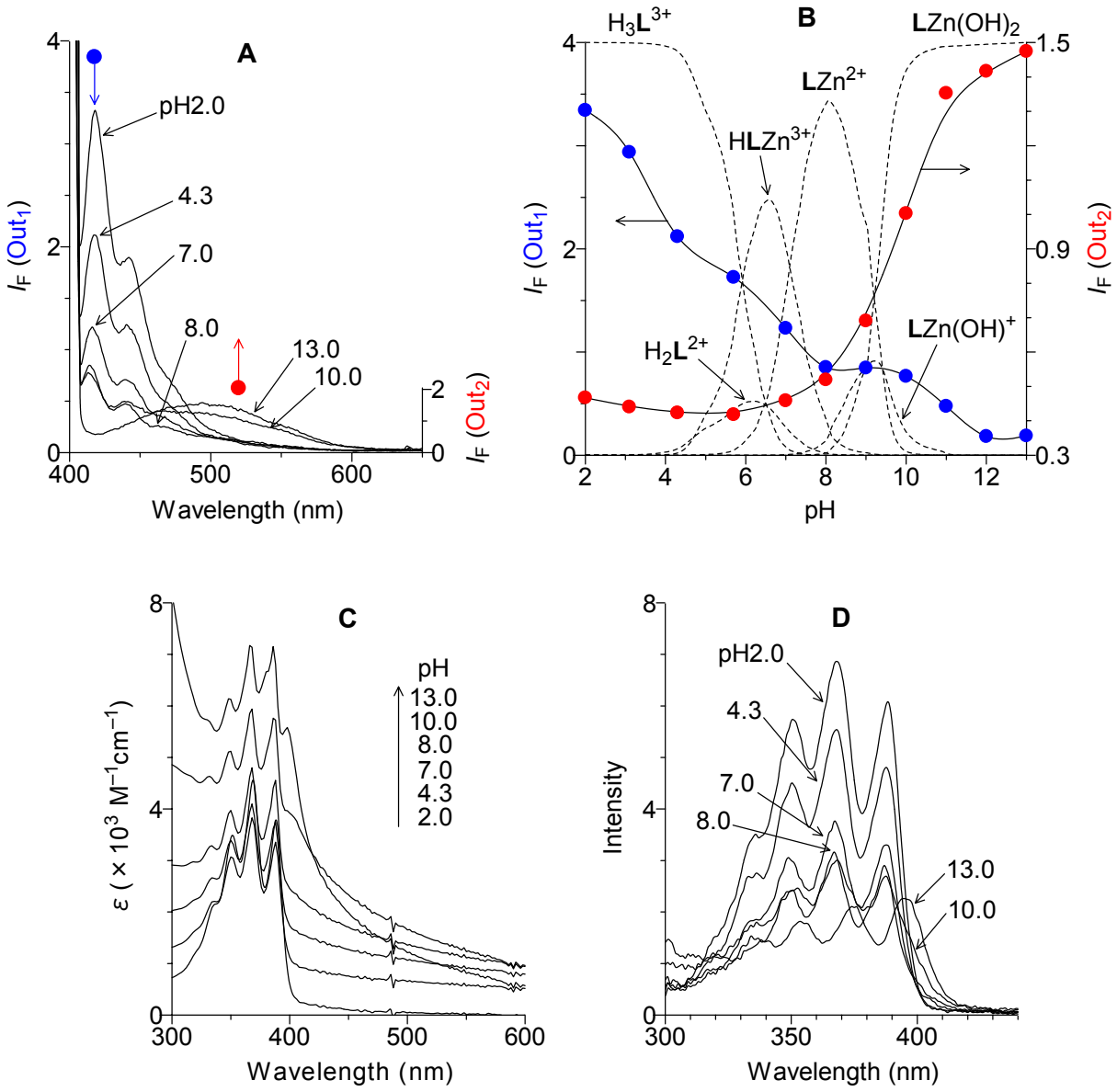


Fig. S1 (**A**) pH-dependent change in fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the presence of 1.0 eq. Zn^{2+} in aqueous NaCl (0.15 M) solution at 298 K. (**B**) Mole fraction distribution of the species and intensities of the fluorescence emissions at λ_{em} = 416 nm [blue: I_F(Out$_1$)] and 520 nm [red: I_F(Out$_2$)]. The emission intensity of **L** in the absence of metals at pH 8 monitoring at 416 nm [I_F(Out$_1$)] is set as 1. The emission intensity of **L** in the absence of metals at pH 10 monitoring at 520 nm [I_F(Out$_2$)] is set as 1. (**C**) Absorption and (**D**) excitation spectra (λ_{em} = 520 nm).

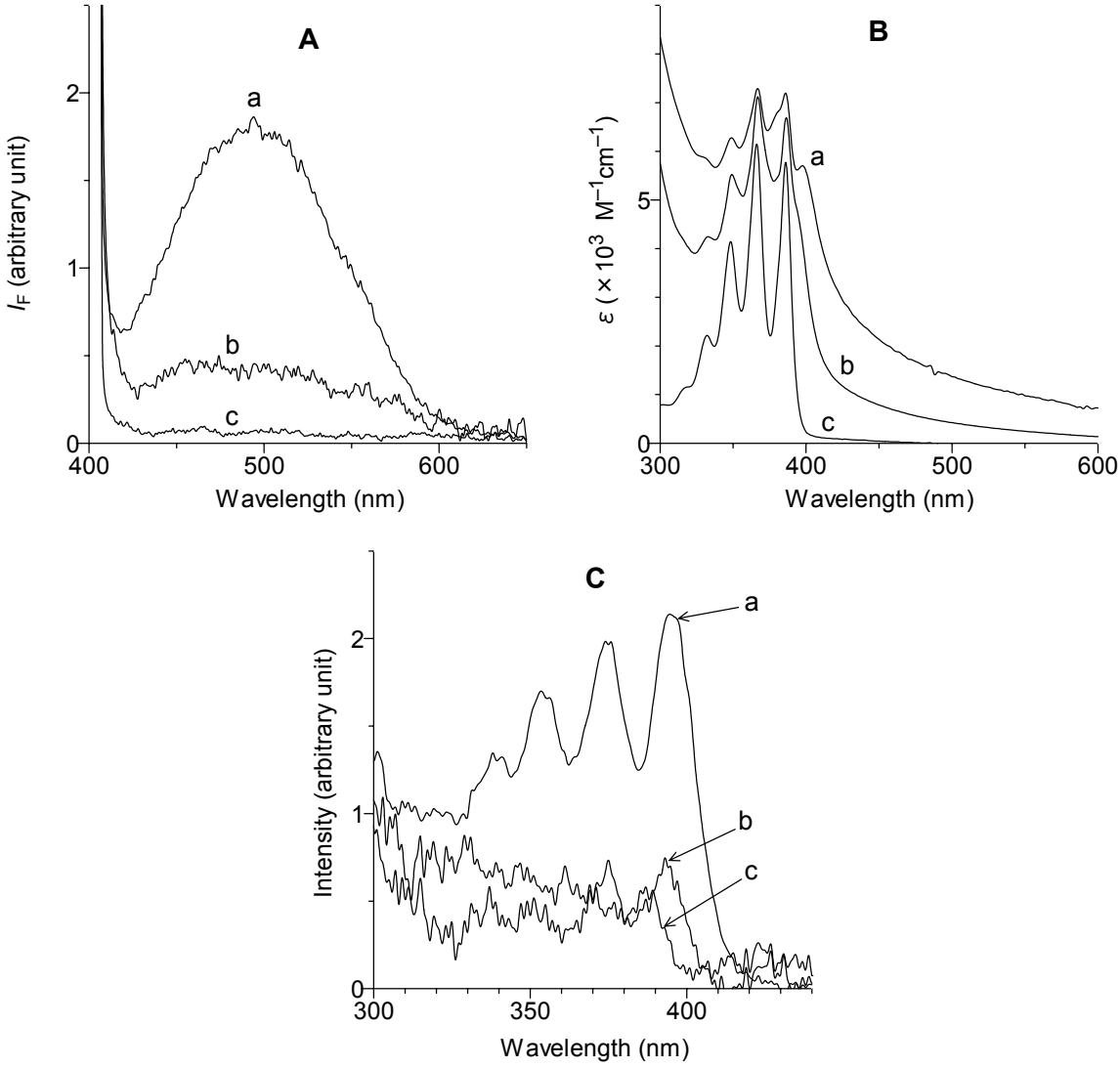


Fig. S2 (**A**) Fluorescence (λ_{ex} = 402 nm), (**B**) absorption, and (**C**) excitation spectra (λ_{em} = 520 nm) of **L** (70 μM) dissolved in various solvents of pH 11.0 at 298 K in the presence of 1.0 eq Zn^{2+}. The respective solvents are: (**a**) water, (**b**) water/acetonitrile (9/1 v/v), and (**c**) water/acetonitrile (1/1 v/v).

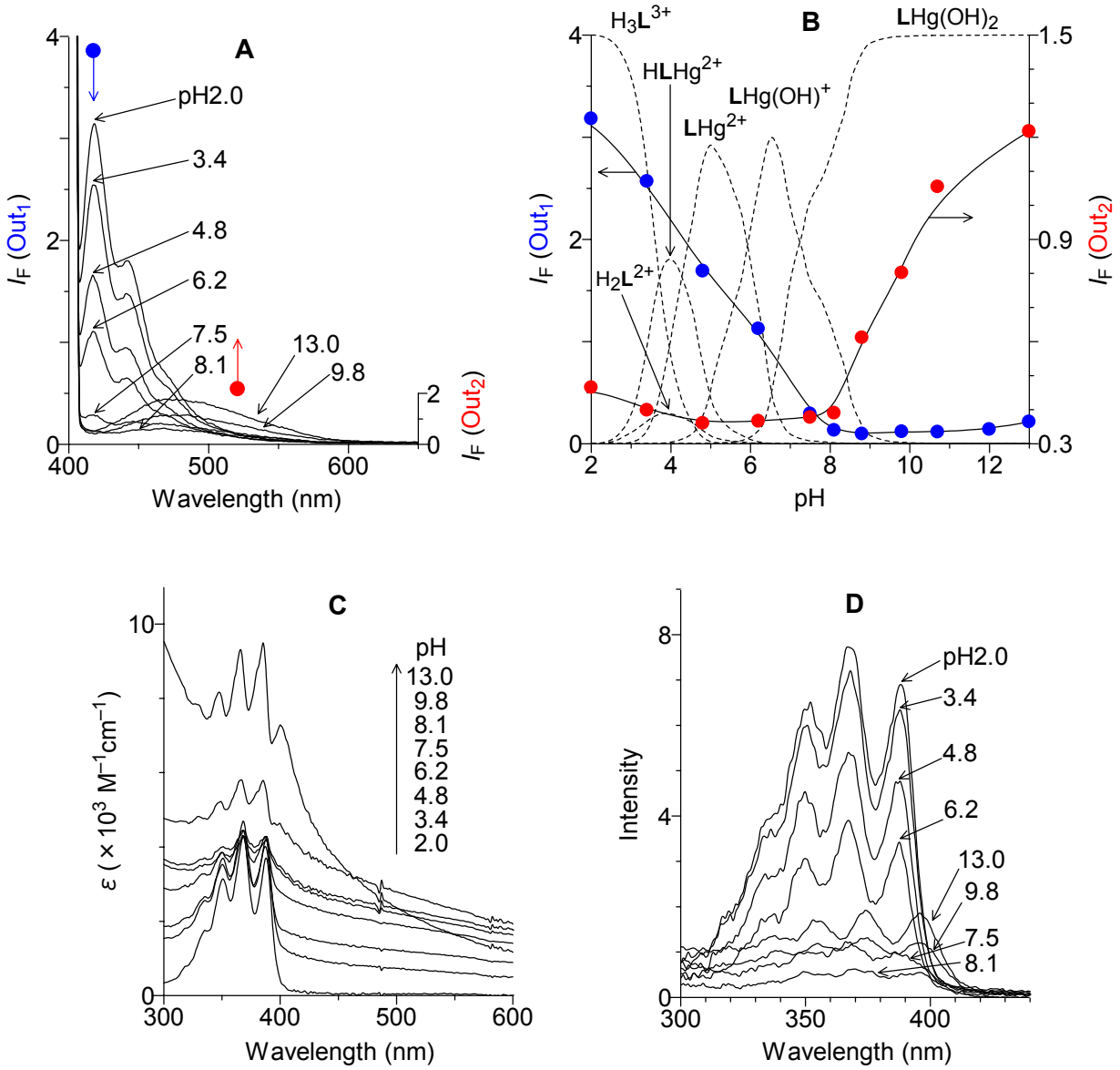


Fig. S3 (**A**) pH-dependent change in fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the presence of 1.0 eq. Hg^{2+} in aqueous NaCl (0.15 M) solution at 298 K. (**B**) Mole fraction distribution of the species and intensities of the fluorescence emissions at λ_{em} = 416 nm [blue: I_F(Out$_1$)] and 520 nm [red: I_F(Out$_2$)]. The emission intensity of **L** in the absence of metals at pH 8 monitoring at 416 nm [I_F(Out$_1$)] is set as 1. The emission intensity of **L** in the absence of metals at pH 10 monitoring at 520 nm [I_F(Out$_2$)] is set as 1. (**C**) Absorption and (**D**) excitation spectra (λ_{em} = 520 nm).

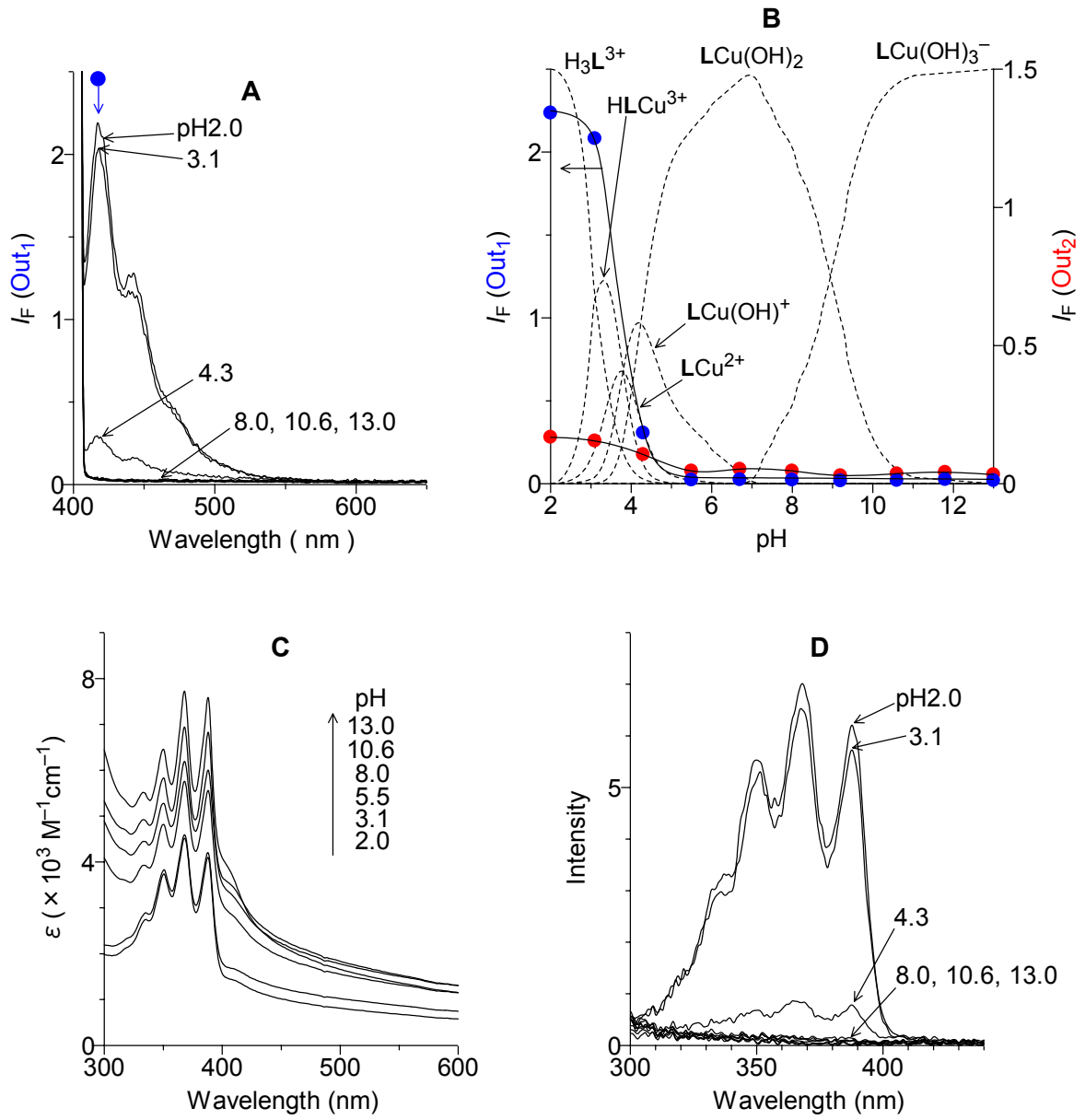


Fig. S4 (**A**) pH-dependent change in fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the presence of 1.0 eq. Cu^{2+} in aqueous NaCl (0.15 M) solution at 298 K. (**B**) Mole fraction distribution of the species and intensities of the fluorescence emissions at λ_{em} = 416 nm [blue: I_F(Out$_1$)] and 520 nm [red: I_F(Out$_2$)]. The emission intensity of **L** in the absence of metals at pH 8 monitoring at 416 nm [I_F(Out$_1$)] is set as 1. The emission intensity of **L** in the absence of metals at pH 10 monitoring at 520 nm [I_F(Out$_2$)] is set as 1. (**C**) Absorption and (**D**) excitation spectra (λ_{em} = 520 nm).

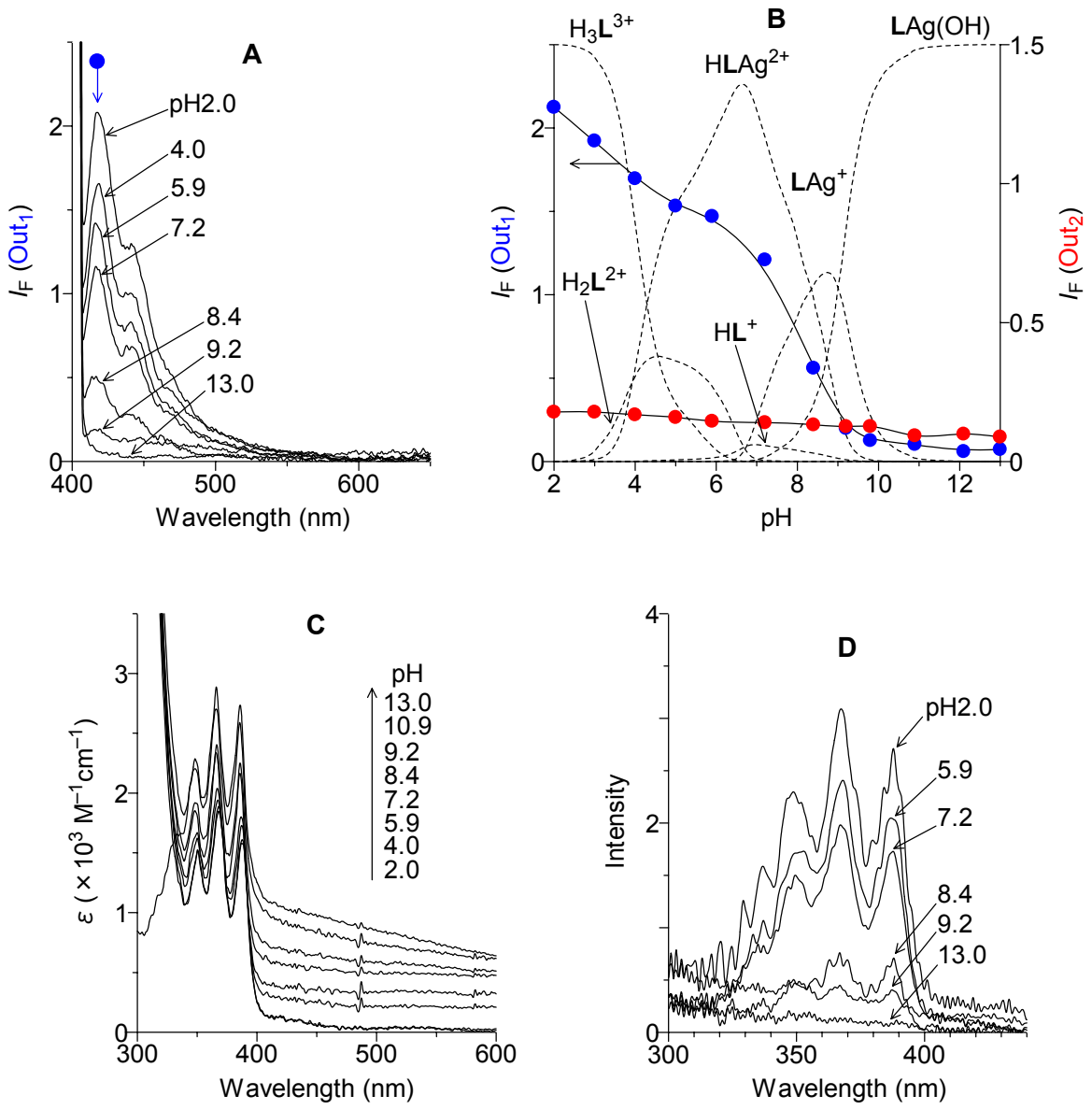
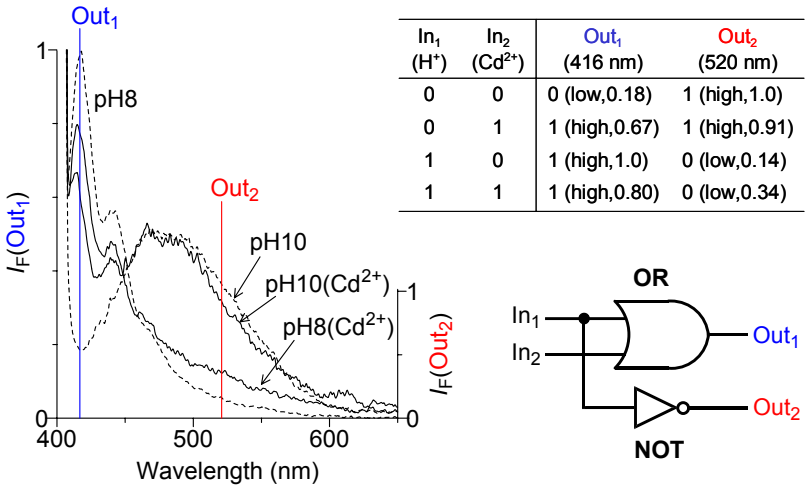
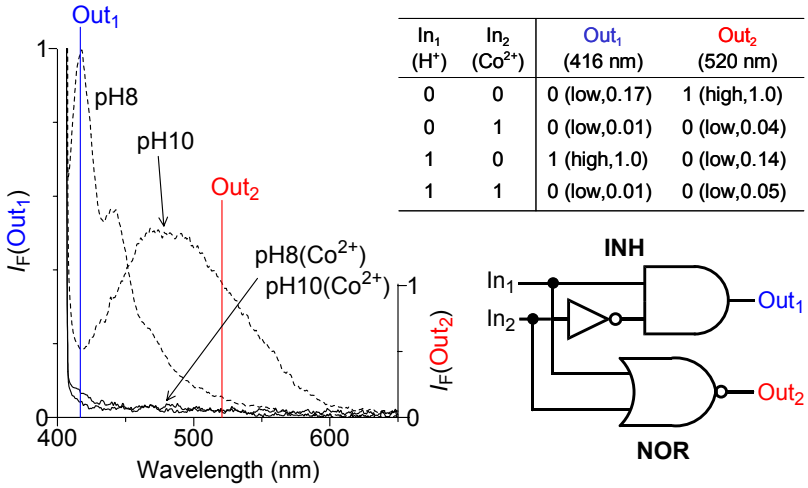


Fig. S5 (**A**) pH-dependent change in fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the presence of 1.0 eq. Ag^+ in aqueous NaCl (0.15 M) solution at 298 K. (**B**) Mole fraction distribution of the species and intensities of the fluorescence emissions at λ_{em} = 416 nm [blue: I_F(Out$_1$)] and 520 nm [red: I_F(Out$_2$)]. The emission intensity of **L** in the absence of metals at pH 8 monitoring at 416 nm [I_F(Out$_1$)] is set as 1. The emission intensity of **L** in the absence of metals at pH 10 monitoring at 520 nm [I_F(Out$_2$)] is set as 1. (**C**) Absorption and (**D**) excitation spectra (λ_{em} = 520 nm).



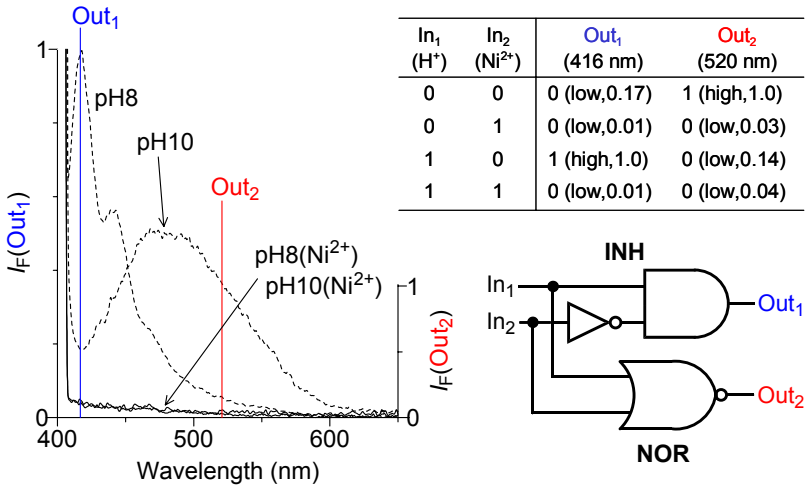
In_1 (H^+)	In_2 (Cd^{2+})	Out_1 (416 nm)	Out_2 (520 nm)
0	0	0 (low,0.18)	1 (high,1.0)
0	1	1 (high,0.67)	1 (high,0.91)
1	0	1 (high,1.0)	0 (low,0.14)
1	1	1 (high,0.80)	0 (low,0.34)

Fig. S6 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Cd^{2+} in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.



In_1 (H^+)	In_2 (Co^{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,0.05)

Fig. S7 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Co^{2+} in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.



In_1 (H^+)	In_2 (Ni^{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,0.03)
1	0	1 (high,1.0)	0 (low,0.14)
1	1	0 (low,0.01)	0 (low,0.04)

Fig. S8 Fluorescence spectra (λ_{ex} = 402 nm) of **L** (70 μM) in the absence and presence of 1 eq. Ni^{2+} in aqueous NaCl (0.15 M) solution at 298 K, truth table, and logic scheme.

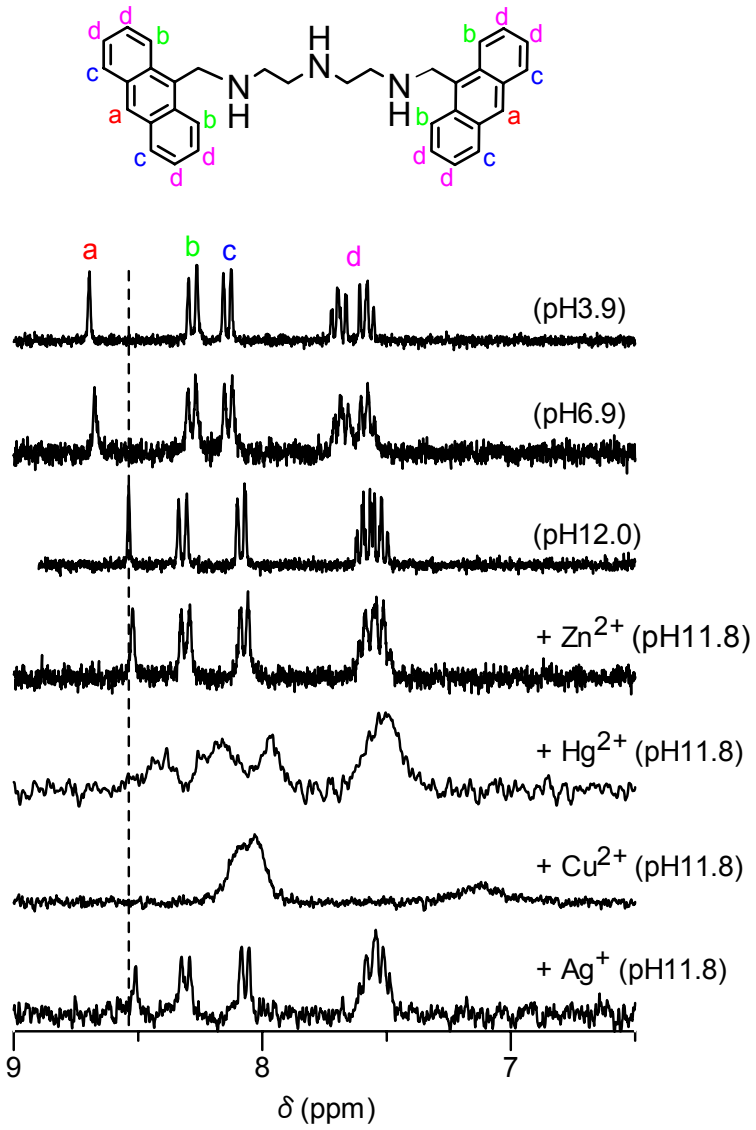


Fig. S9 ^{1}H NMR spectra of **L** obtained in the absence and presence of metal cations (1 eq.) in D_2O (pH = pD – 0.4).