Electronic Supplementary Information (ESI)

Selective Ammonia Sensing through Reversible Vapochromism and Luminescence ON–OFF Switching of a Chalcone-Based Co(II) Complex

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EXPERIMENTAL SECTION

Synthesis. All reagents were commercially available and used without further purification.

Synthesis of 3-[4-(Dimethylamino)phenyl]-1-(2-pyridinyl)-2-propen-1-one (***L1***). 2-acetylpyridine (6.057 g, 50 mmol) and 4-Dimethylaminobenzaldehyde (7.460 g, 50 mmol) were stirred in MeOH (250 mL) at room temperature. To the solution was added 0.5 M NaOH aq. (110 mL) and stirred at room temperature for further 24 hours. The orange precipitate was collected by filtration, washed with MeOH, and dried in vacuum to give **L1** (5.006 g, 39.7 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.74 (d,1H), 8.19 (t, 1H), 8.06 (d, 1H), 7.94 (d, 1H), 7.85 (t, 2H), 7.65 (d, 2H), 7.45 (d, 1H), 6.65 (d, 2H), 3.0 (s, 6H) ppm.

*Synthesis of complex **L1·Co**.* A quantity of **L1** (0.4772 g, 1.80 mmol) was dissolved in acetone (200 mL) after which a solution of $CoCl_2 \cdot 6H_2O$ (0.2250 g, 0.946 mmol) was added to the solution. The solution immediately turned to dark red color. The solution was then stirred for further 24 h at room temperature. The precipitate was collected by filtration and washed with a small amount of acetone to give **L1·Co** (0.2776 g, 92.2%). Calcd. for **L1·Co·0.5acetone·0.5H_2O**: H 5.38, C 59.84, N 8.24.; Found: H 5.40, C 59.83, N 8.33.

Physical measurements. ^{1}H-NMR spectra were acquired with a Bruker AVANCE NEO 400 instrument operating at 400 MHz, using the deuterated solvent to provide the lock signal and residual solvent tetramethylsilane (TMS) as the internal reference. Elemental analyses for C, H and N were carried out at the Instrumental Analysis Centre of Josai University. SC-XRD measurements were recorded on an Oxford Gemini Ultra diffractometer employing graphite monochromated Mo Kα radiation generated from a sealed tube (λ = 0.7107 Å). Data integration and reduction were undertaken with APEX4 program. The structures were solved by Olex2 with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. Hydrogen atoms were included in idealized positions and refined using a riding model. Photoluminescence lifetime was measured using a Quantaurus-Tau fluorescence lifetime measurement system (C16361-01 Hamamatsu Photonics, Japan).

Table S1 Crystal parameters for **L1·Co**.

Formula	$C_{32}H_{32}CoCl_2N_4O_2$
T/K	100
Crystal system	orthorhombic
Space group	*Pbcn*
a / Å	12.8863(7)
b / Å	10.2693(6)
c / Å	21.4852(12)
V / *Å*^{3}	2843.2(3)
Z	4
GOF	1.066
R1	0.0238
wR2	0.0622
CCDC number	2512162

Table S2 Elemental analysis of **L1·Co** under various condition.

	C Found (calc.)	H Found (calc.)	N Found (calc.)
L1·Co (+0.5H_2O, +0.5acetone)	59.84 (59.83)	5.38 (5.40)	8.24 (8.33)
L1·Co@NH_3 (+H_2O, +5.5NH_3)	51.11 (51.51)	6.58 (6. 82)	18.1 (17.83)
re-L1·Co dried for 3 h (+1.8H_2O, +2.8NH_3)	53.89 (53.79)	6.00 (6.21)	13.52 (13.33)
re-L1·Co dried for 1 day (+1.8H_2O, +2.8NH_3)	53.58 (53.79)	5.88 (6.21)	13.10 (13.33)
re-L1·Co dried for 3 days (+1.8H_2O, +2.8NH_3)	53.77 (53.79)	5.95 (6.21)	13.12 (13.33)
L1·Co@NH_3 after heating (+0.5H_2O, +0.5NH_3)	58. 68 (58.95)	4.99 (5.33)	9.47 (9.67)

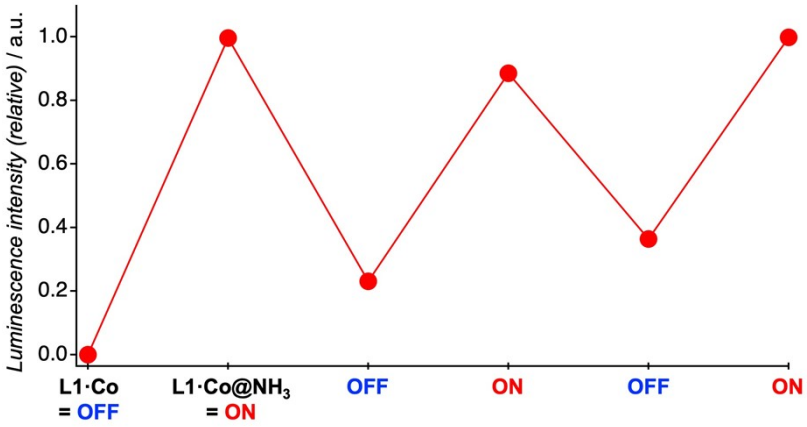

Fig. S1 Reversible luminescence ON–OFF behavior of **L1·Co** upon repeated exposure to NH_3 vapor and subsequent air-drying.

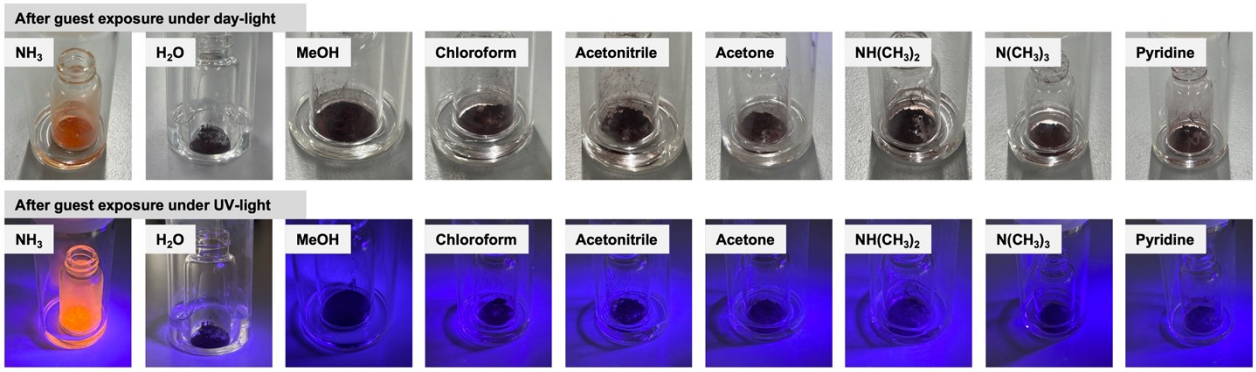

Fig. S2 Photograph of **L1·Co** under water vapor and various organic solvent vapor. (Top) Under day-light and (bottom) under UV-light.

Fig. S3 The isodensity plots of the frontier orbitals of **L1**.

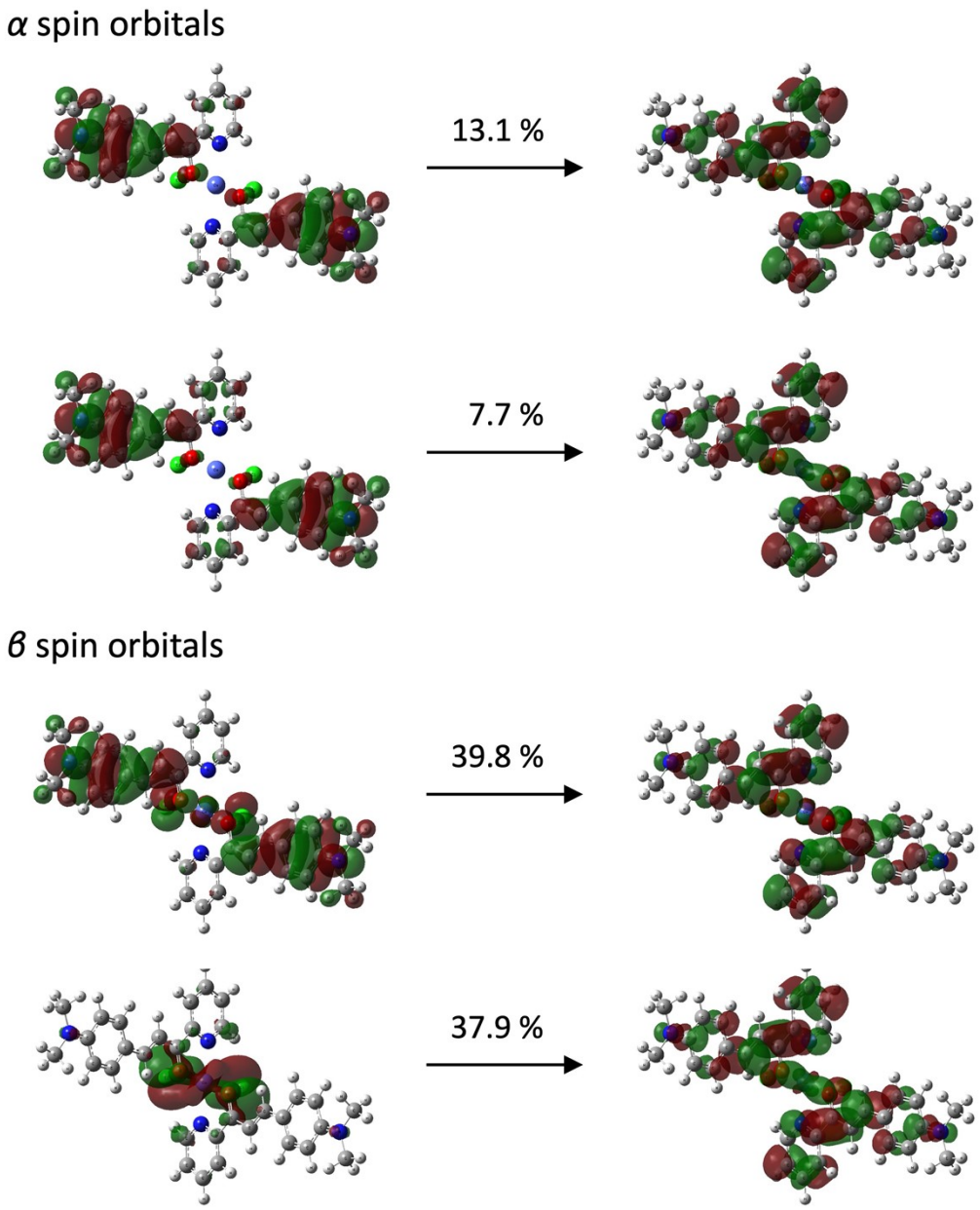

Fig. S4 The selected natural transition orbital (NTO) analysis of **L1·Co**.

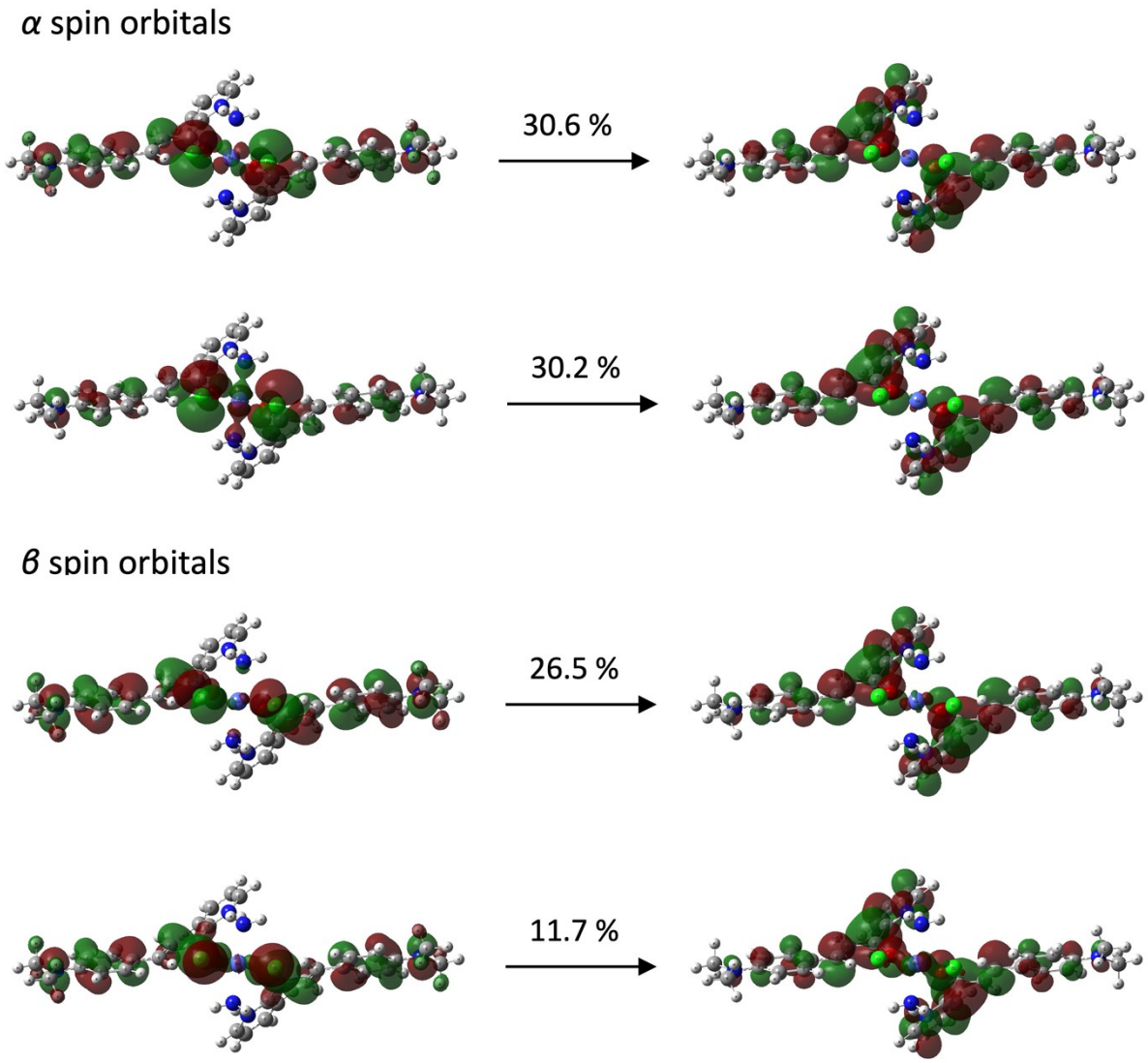

Fig. S5 The selected natural transition orbital (NTO) analysis of **L1·Co@NH_3**.

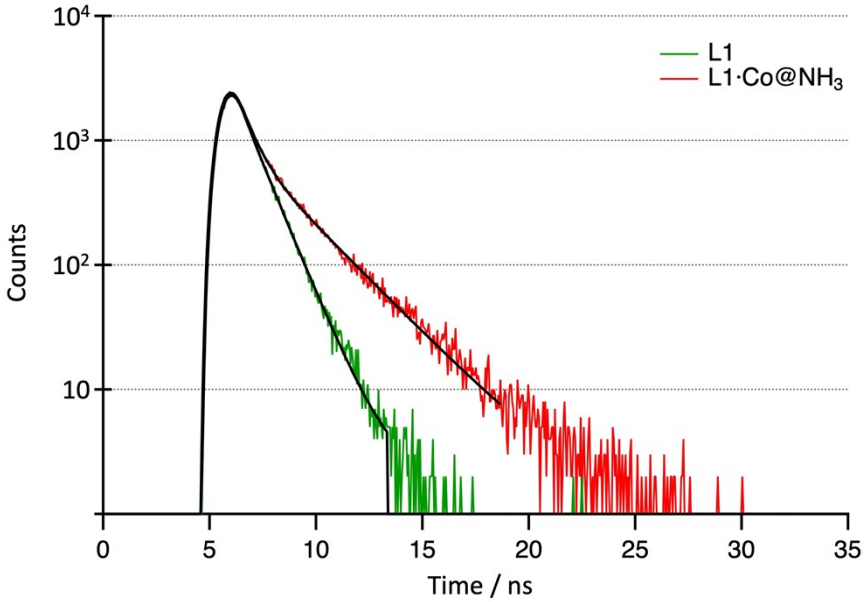

Fig. S6 Luminescence decay profiles of the chalcone-based ligand **L1** (green) and the Co(II) complex after exposure to ammonia vapor, **L1·Co@NH$_3$** (red).

Table S3 Luminescence lifetime and relative parameters for **L1** and **L1·Co**.

	τ_1 (ns)	τ_2 (ns)	χ^2
L1	0.34	1.06	0.988
L1·Co	0.55	2.51	1.154

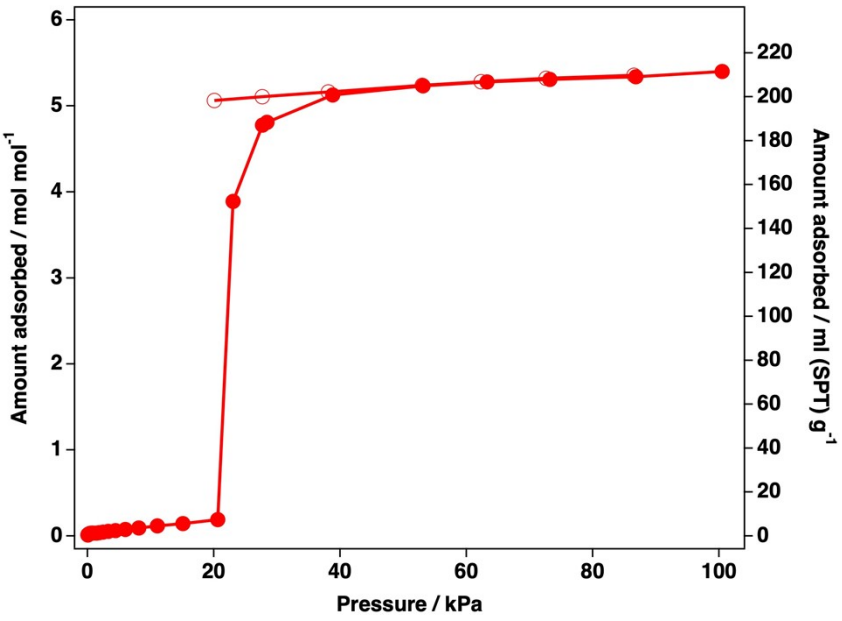

Fig. S7 NH_3 gas adsorption (closed) and desorption (open) isotherms for **L1·Co** measured at 25 °C.

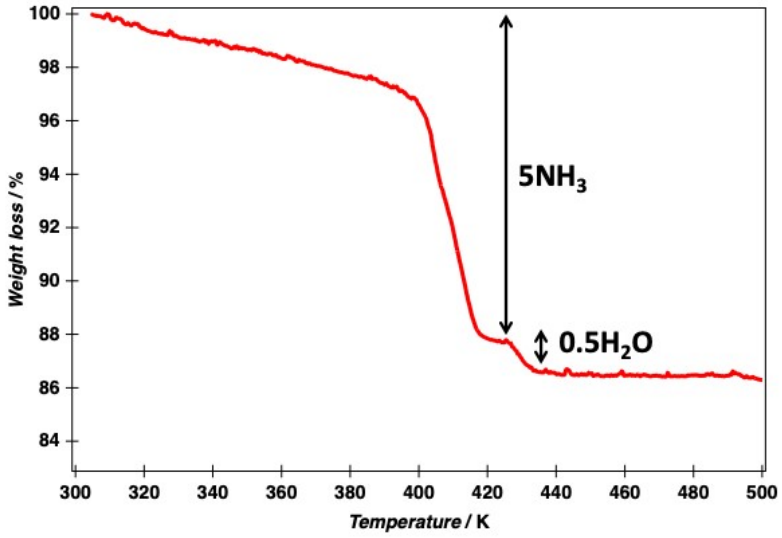

Fig. S8 TGA for **L1·Co@NH_3**. The scan rate is 5K/min.