Fluorescence behaviour of an anthracene-BODIPY system affected by spin states of a dioxolene-cobalt centre

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Supplementary Information Data

IR spectra of complexes **1** and **2** and H_2L, absorption spectra of H_2L, cyclic voltammograms of **1**, **2**, **1'**, and **2'**, ^1H NMR spectra of **1, 2** and **1'**, fluorescence spectra of **1'**, H_2L and H_2L', and ^1H NMR spectra of (**i**), (**ii**) and H_2L are presented as supplementary information.

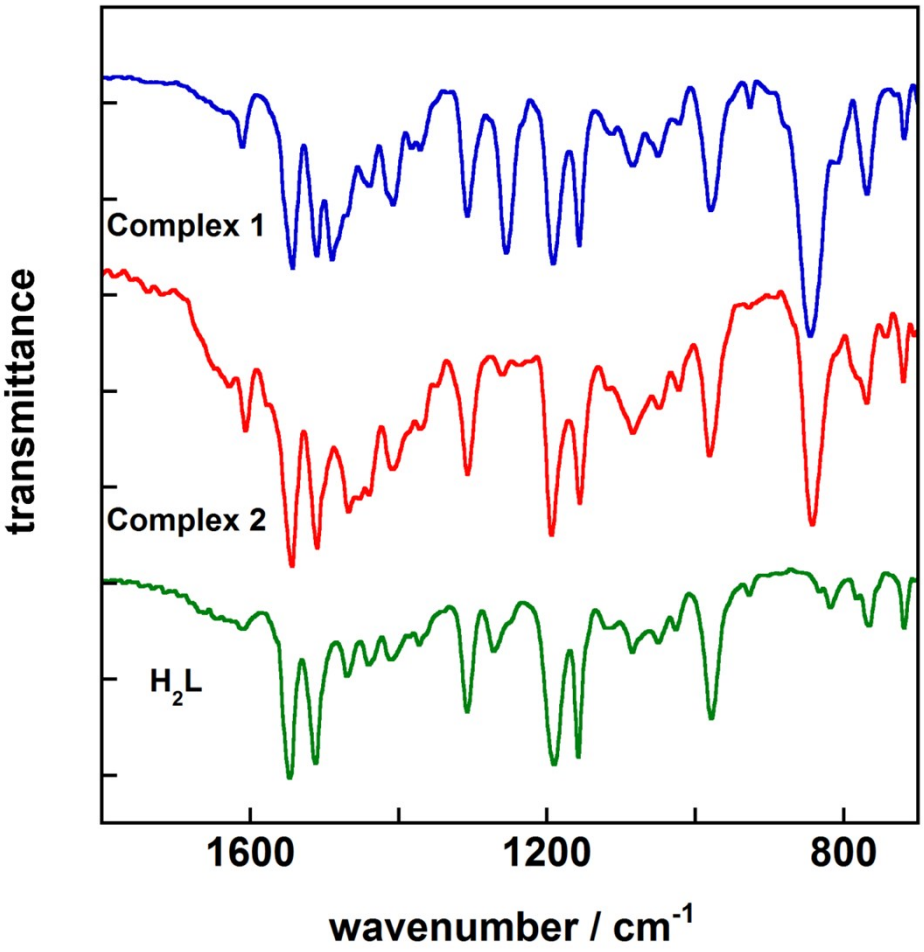

Fig. S1 IR spectra of complexes **1** and **2** and H_2L.

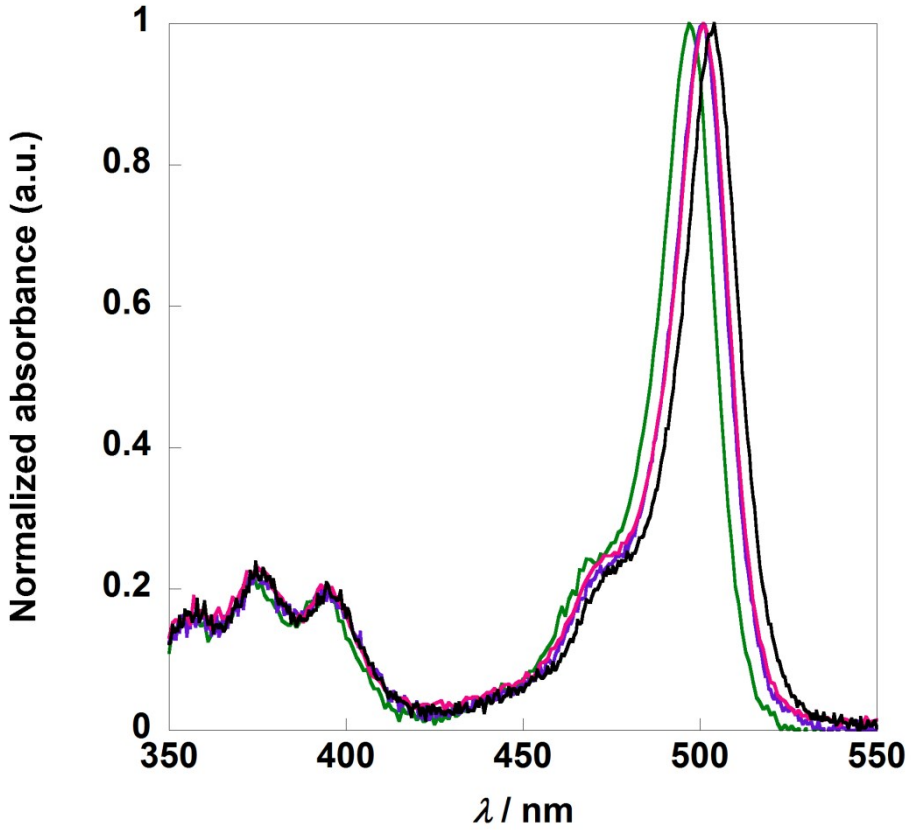

Fig. S2 Normalized absorption spectra of H_2L in several solutions: CH_3CN, (—); CH_2Cl_2, (—); toluene, (—); THF, (—).

Table S1 Photophysical properties of H_2L, and complexes **1** and **2** in several solvents.

		λ_{abs} (max/nm)[a]	λ_{abs} (max/nm)[b]	λ_{em} (max/nm)	Φ_{ex350}[c]	Φ_{ex465}[c]
Complex **1**	CH_3CN	373	497	509	0.003	0.005
Complex **2**	CH_3CN	373	497	509	0.020	0.027
H_2L	CH_3CN	374	497	509	0.030±0.006	0.038
	CH_2Cl_2	375	501	512	0.42±0.08	0.39
	Toluene	375	504	515 (435)[d]	0.57±0.07	0.55
	THF	375	501	511	—	—

[a]The anthracene moiety. [b]The BODIPY moiety. [c]The fluorescence quantum yields were determined using fluorescein as a standard (Φ= 0.85 in carbonate-bicarbonate buffer at a pH of about 9.6) [d]Fluorescence band was observed in toluene at excitation at 350 nm.

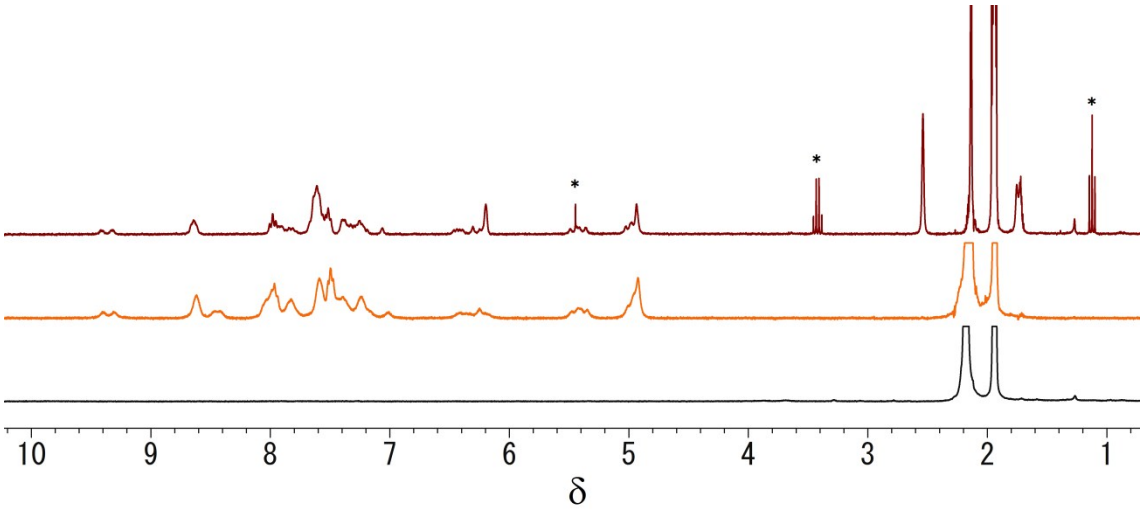

Fig. S3 ^{1}H NMR spectra (300 MHz, CD_3CN) of complexes **1** (top), **1'** (middle) and **2** (bottom) (* solvent).

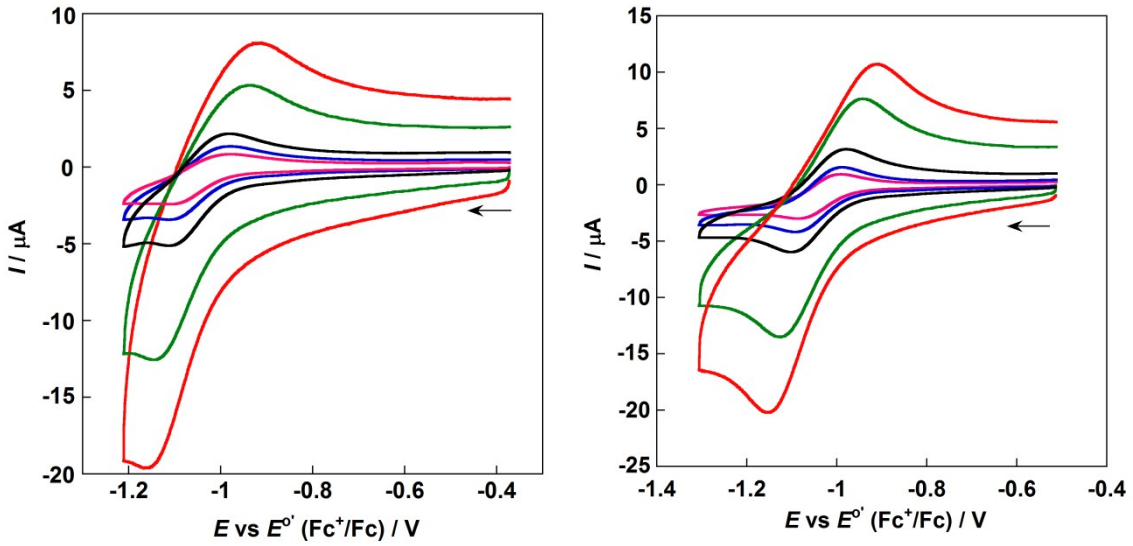

Fig. S4 The reduction processes of complexes **1** (left) and **1'** (right) in CH_3CN containing 0.10 M Bu_4NPF_6 recorded at scan rates of 25 (—), 50 (—), 100 (—), 500 (—), and 1000 (—) mV s^{-1}: working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).

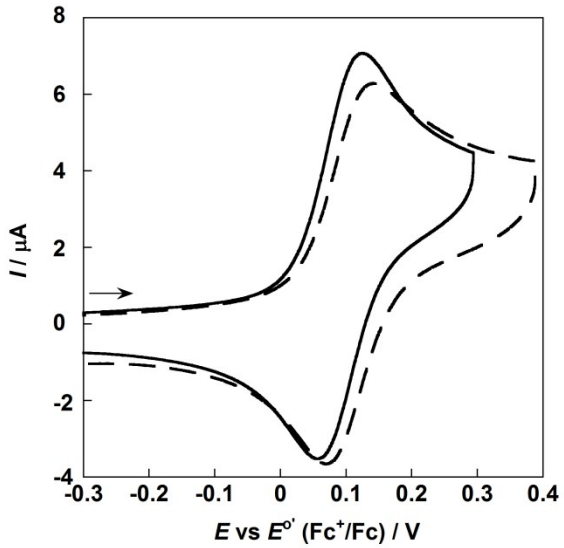

Fig. S5 The oxidation processes of complexes **1** (– –) and **1'** (—) in CH_3CN containing 0.10 M Bu_4NPF_6 recorded at a scan rate of 100 mV s^{-1}: working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).

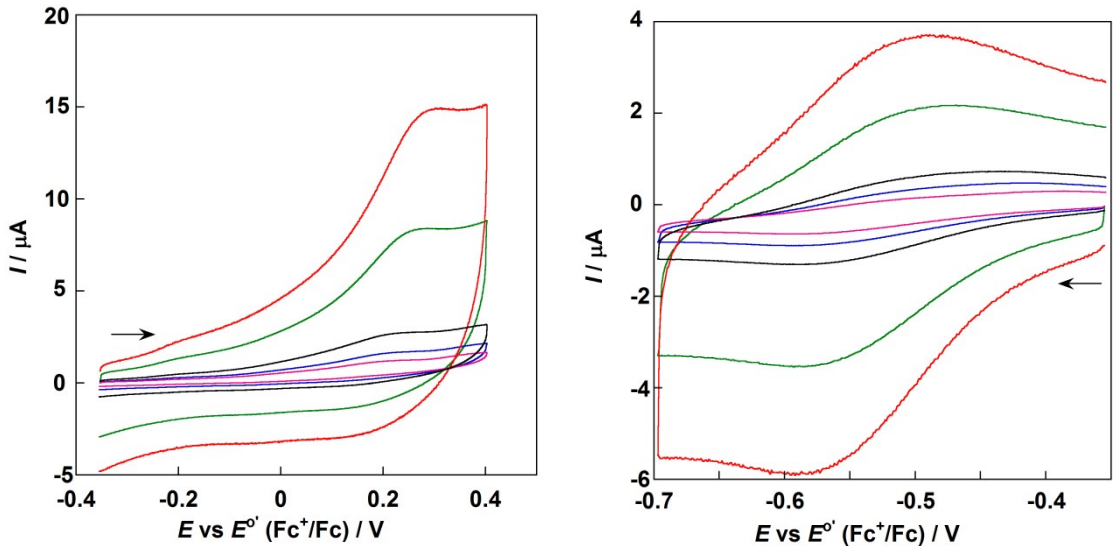

Fig. S6 The oxidation (left) and reduction (right) processes of complex **2** in CH_3CN containing 0.10 M Bu_4NPF_6 recorded at scan rates of 25 (—), 50 (—), 100 (—), 500 (—), and 1000 (—) mV s^{-1}: working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).

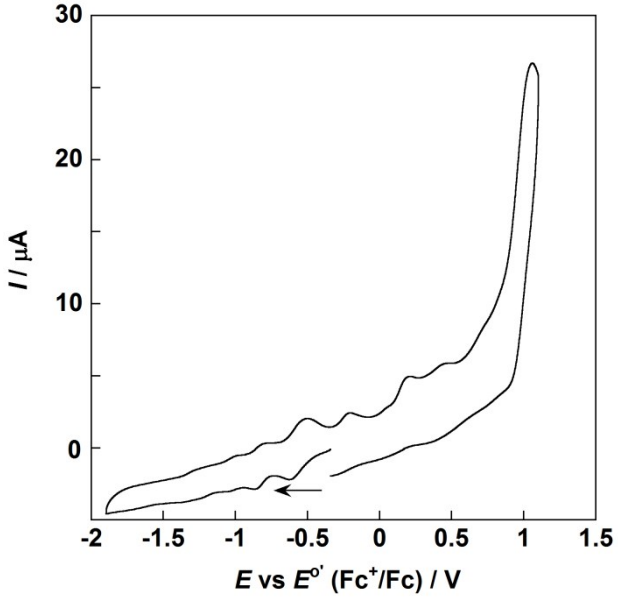

Fig. S7 Cyclic voltammogram of **2'** (—) in CH_3CN containing 0.10 M Bu_4NPF_6 recorded at a scan rate of 100 mV s^{-1}: working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).

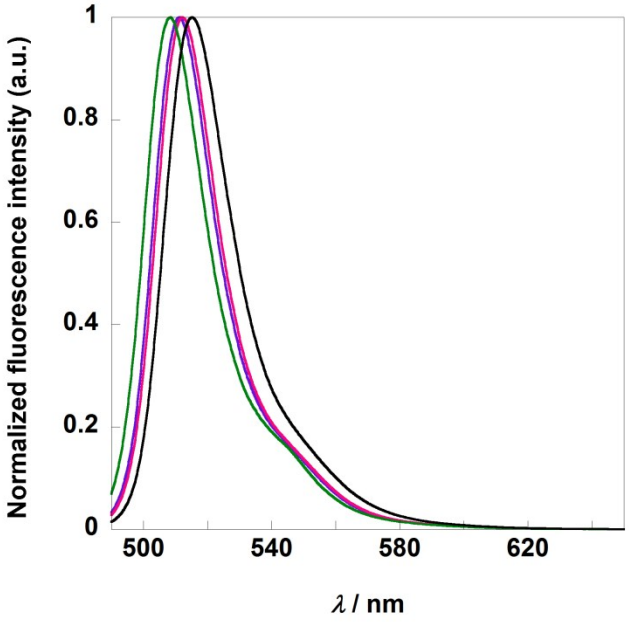

Fig. S8 Normalized fluorescence spectra of H_2L in several solutions: CH_3CN, (—); CH_2Cl_2, (—); toluene, (—); THF, (—). Excitation wavelength = 470 nm.

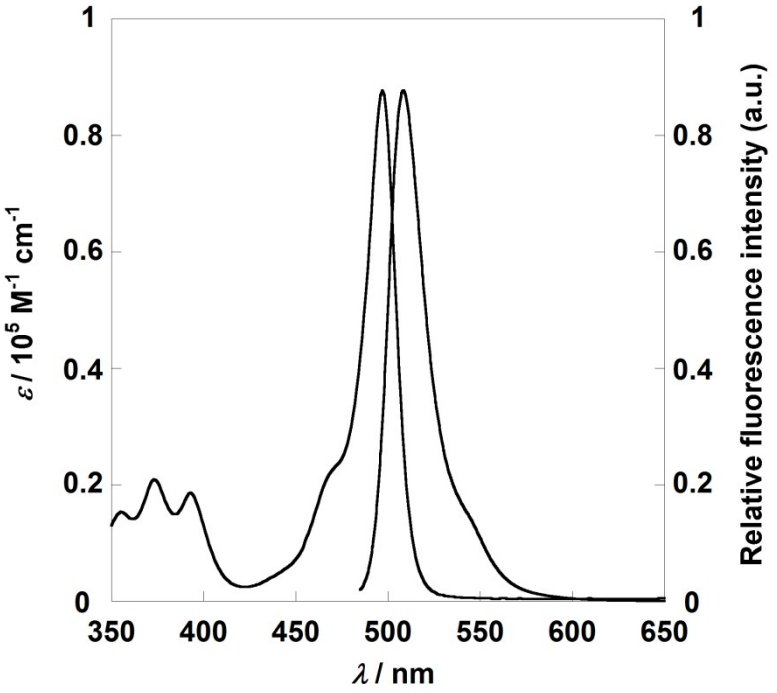

Fig. S9 Absorption and fluorescence spectra of H_2L in CH_3CN.

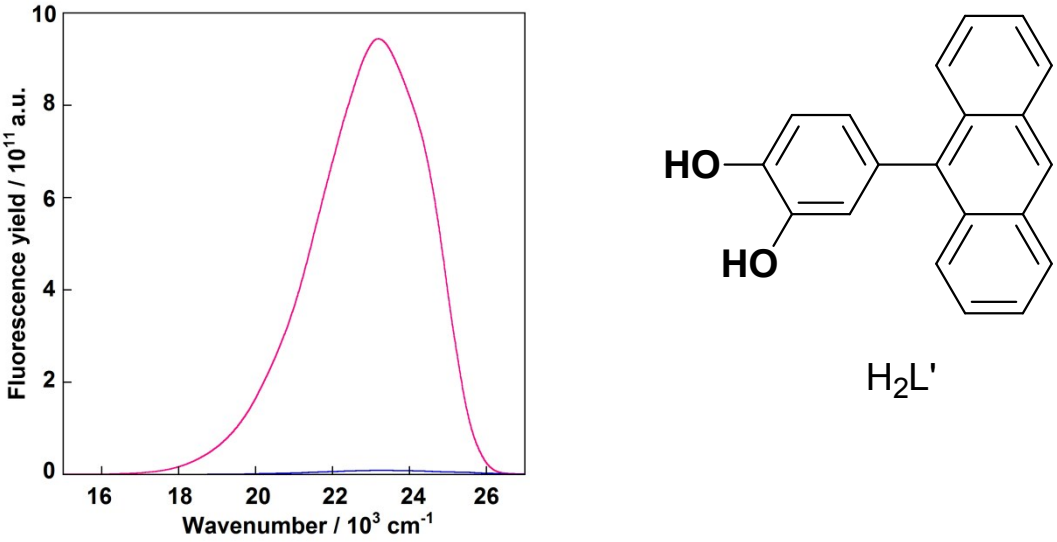

Fig. S10 Fluorescence spectra of **H_2L'** (—), complex **1'** (—) in 350 nm excitation wavelength. Solvent: CH_3CN.

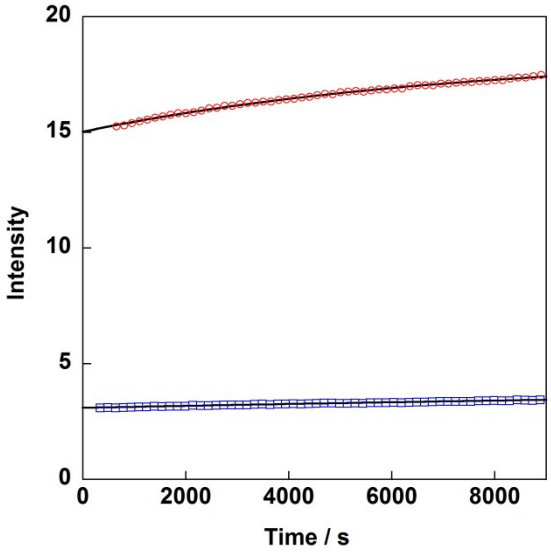

Fig. S11 Time variations of fluorescence intensity of complexes **1** (□) and **2** (○); λ_{ex} = 470 nm, maximum fluorescence intensity (508 nm monitored) of emission spectra in CH_3CN over 9000 s.

$$[Co(L)] \xrightarrow{k_d} [Co] + L$$

Scheme S1. A simple model for ligand dissociation.

$$[Int] = [Int]_0 + C[1-\exp(-k_d t)] \quad \text{(S1)}$$

The [Int], $[Int]_0$, C, k_d, and t represent the fluorescence intensity, the deduced stating value, the species dependent value, the dissociation rate constant, and time, respectively

Table S2 The obtained values by using equation (S1).

	$[Int]_0$	C	k_d	R^2
Complex **1**	3.10	1.49	2.93×10^{-5} s^{-1}	0.98677
Complex **2**	15.0	3.36	1.38×10^{-4} s^{-1}	0.99706

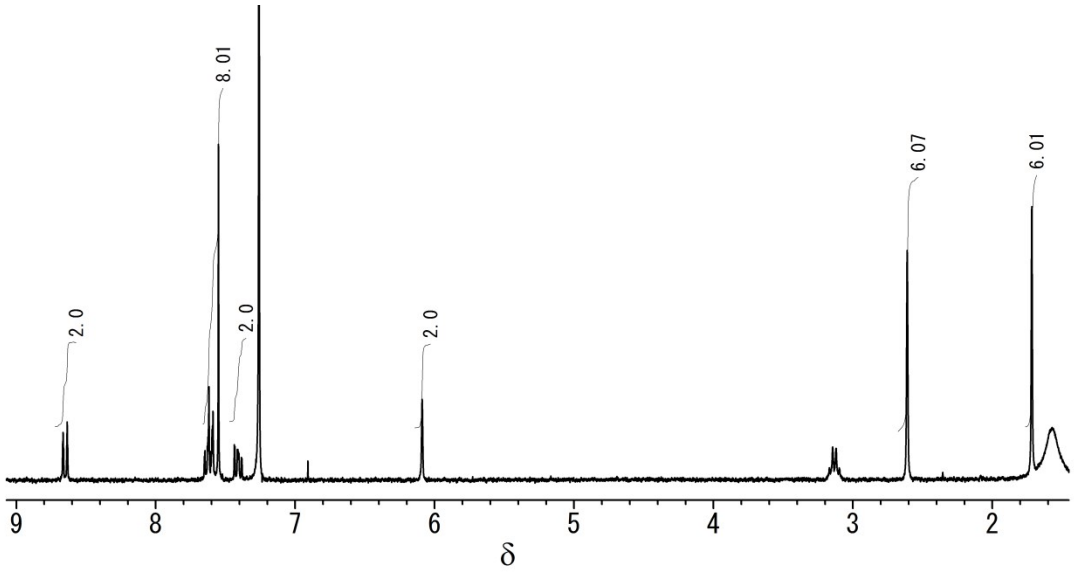

Fig. S12 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (**i**).

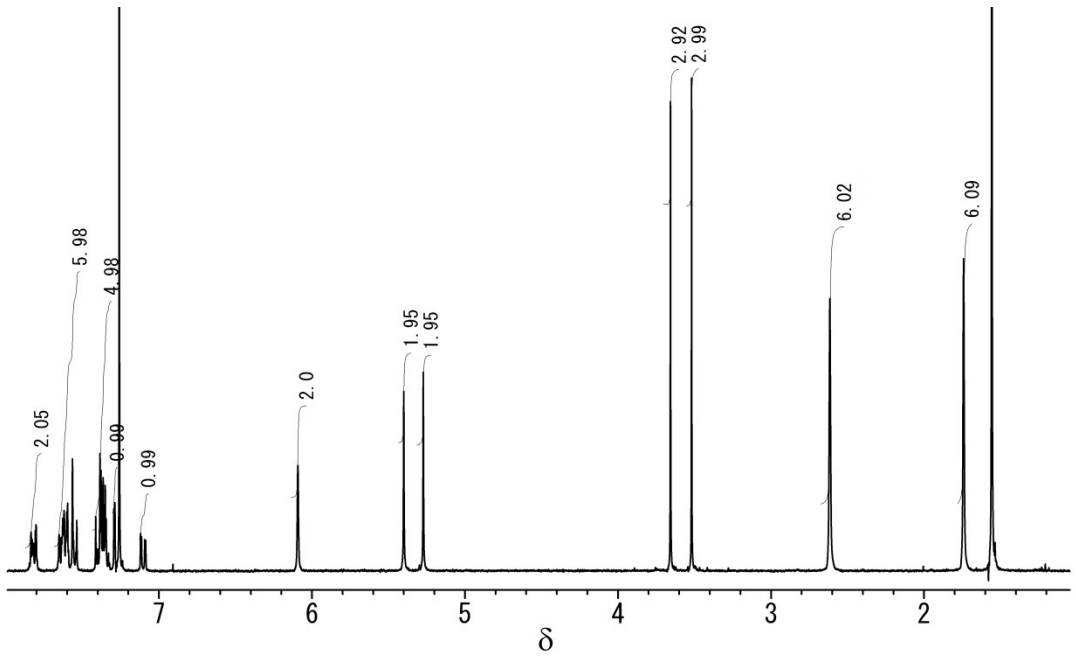

Fig. S13 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (**ii**).

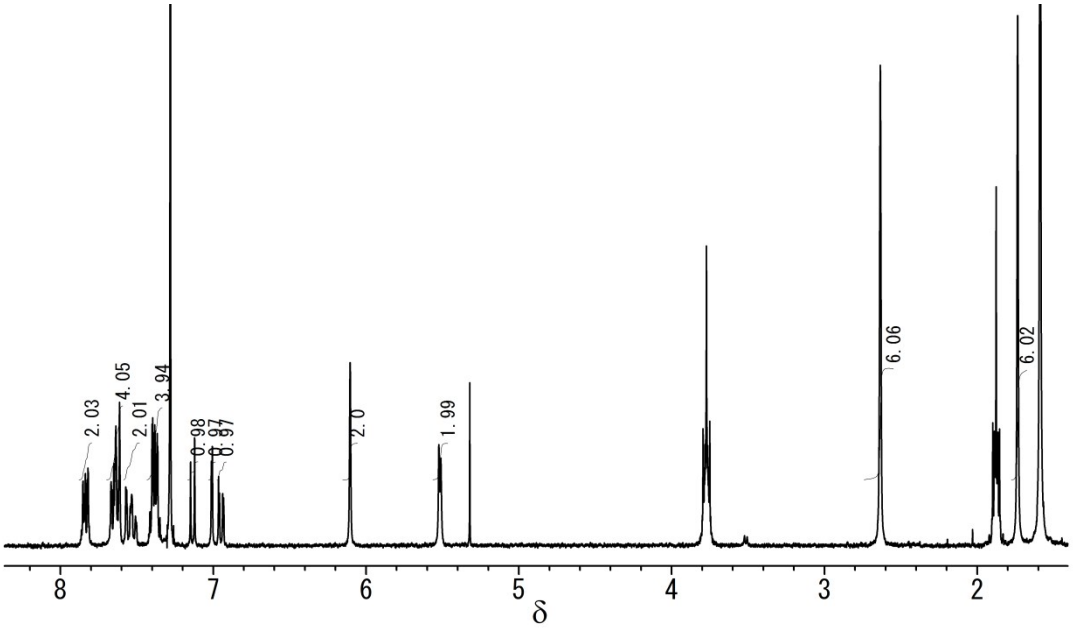

Fig. S14 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of H_2L.

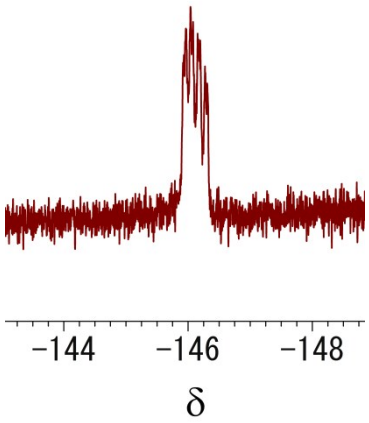

Fig. S15 ^{19}F NMR spectrum (282.4 MHz, $CDCl_3$) of H_2L.