Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Water-soluble Copper(I) Complexes Bearing 2,2'-Bicinchoninic Acid Dipotassium Salt with Red-light Absorption and Repeatable Colour Change upon Freezing Operation

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Preparation

Preparation of complex **2**. The complex was prepared by modified method described above using DMSO (10 mL), 2,2'-bicinchoninic acid disodium salt ($BCANa_2$) (194.11 mg, 0.5 mmol), $[Cu(MeCN)_4]PF_6$ (93.19 mg, 0.25 mmol), and acetone (150 mL). Purple powder, yield 194.48 mg. ^{1}H MNR (500 MHz, D_2O) δ = 8.84 (*s*, 4H), 8.20 (*d*, 4H, *J* = 8 Hz), 7.81 (*d*, 4H, *J* = 9 Hz), 7.57 (*t*, 4H, *J* = 8 Hz), 7.31 (*t*, 4H, *J* = 8 Hz).

Preparation of complex **3**. The complex was prepared by modified method described in literature and mentions above. Under argon atmosphere, 2,2'-bicinchoninic acid (346 mg, 1 mmol) in DMSO (25 mL) was added by tetrakis(acetonitrile)copper(I) hexafluorophosphate (186 mg, 0.5 mmol) at room temperature. The solution is added by dichloromethane (300 mL), and refrigerator. The solvent was evaporated, and acetone (20 mL) was added into the residue. Then, diethyl ether (170 mL) was added. The formed precipitation was collected by filtration and dried. Yield 449.0 mg. Elemental analysis found: C, 51.62%; H, 3.26%; N, 5.74%. Calcd for $C_{40}H_{24}N_4O_8CuPF_6 \cdot 2H_2O$ C, 51.48%; H, 3.02%; N, 6.00%. ^{1}H MNR (500 MHz, acetone-d_6) δ = 9.61 (*s*, 4H), 8.91 (*d*, 4H, *J*=8.0 Hz), 8.14 (*d*, 4H, *J*=8.5 Hz), 7.74 (*t*, 4H, *J*=7.25 Hz), 7.48 (*t*, 4H, 8.25 Hz)

Preparation of complex **4**. The complex was prepared by modified method described in literature and mentions above. Under argon atmosphere, acetone 15 mL was added by ^{1}H MNR (500 MHz, acetone-d_6) δ = 9.15 (*d*, 4H, *J*=8.5 Hz), 9.03 (*d*, 4H, *J*=8.5 Hz), 8.19 (*d*, 4H, *J*=7.5 Hz), 7.92 (*d*, 4H, *J*=8.5 Hz), 7.62 (*t*, 4H, *J*=8.0 Hz), 7.43 (*t*, 4H, *J*=8.5 Hz).

Table S1. Experimental and calculated results of elemental analysis for the powder of **1**.

	Carbon / %	**Hydrogen / %**	**Nitrogen / %**
Found	51.36	3.09	5.82
Calculated for $K_4[Cu(biq(COO)_2)_2]PF_6$	45.75	1.92	5.34
Calculated for $K_4[Cu(biq(COO)_2)_2]PF_6 \cdot 4H_2O$	42.81	2.51	4.99
Calculated for $K_3[Cu(biq(COO)_2)_2]$	55.49	2.33	6.47
Calculated for $K_3[Cu(biq(COO)_2)_2] \cdot 4H_2O$	51.25	3.01	5.98

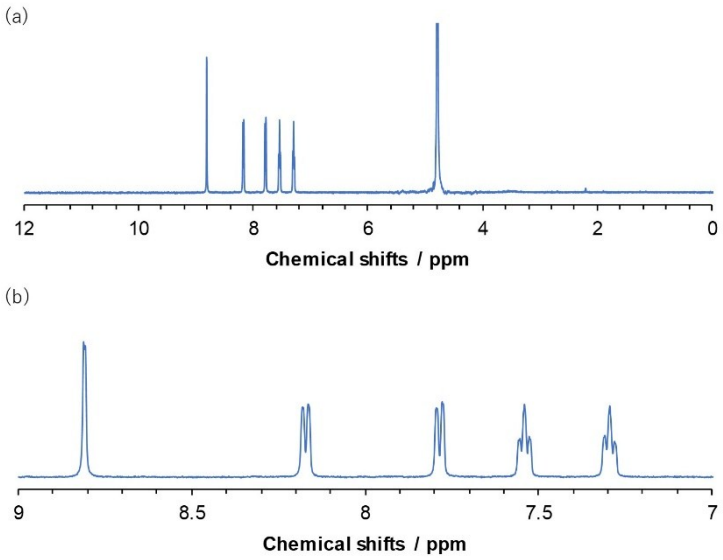

Figure S1. (a) The ^{1}H NMR spectrum of D_2O solution of **1** at room temperature under air. (b) The partial ^{1}H NMR spectrum of (a).

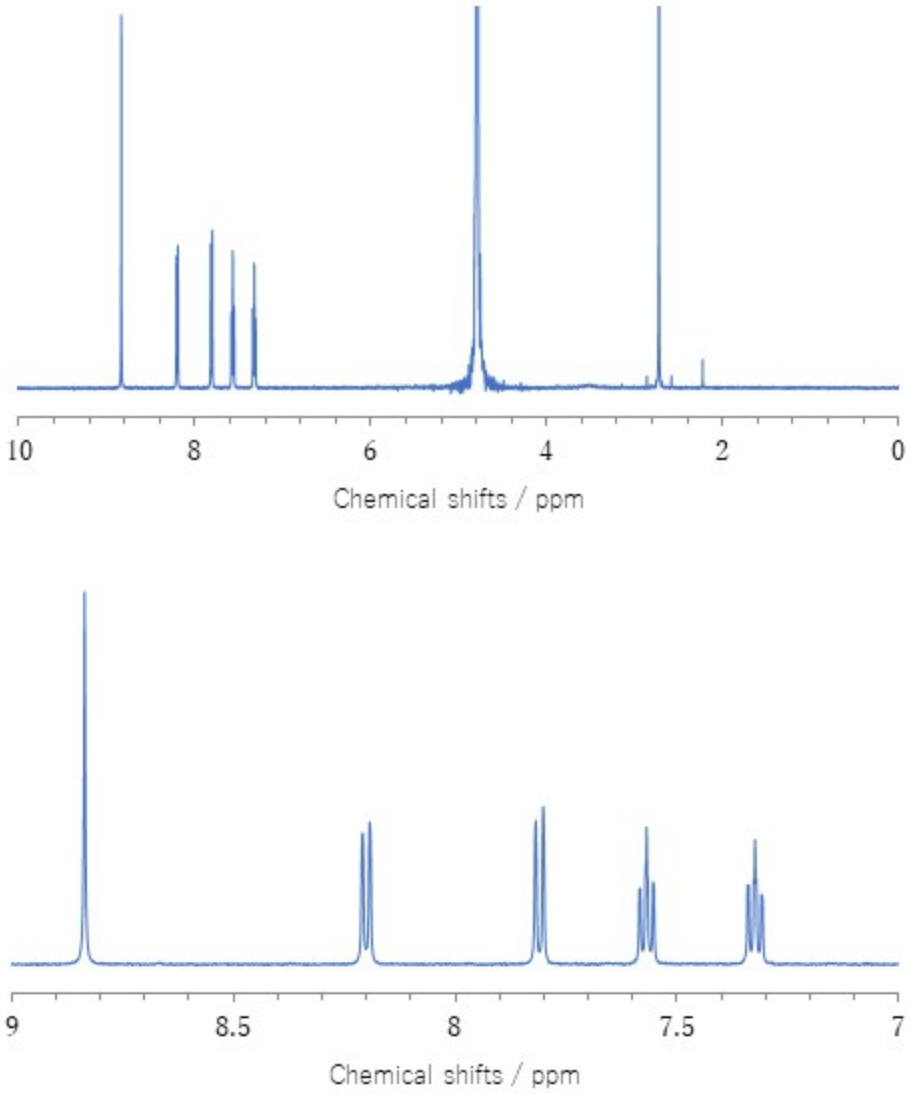

Figure S2. (top) The ^{1}H NMR spectrum of D_2O solution of **2** at room temperature under air. (b) The partial ^{1}H NMR spectrum of (a).

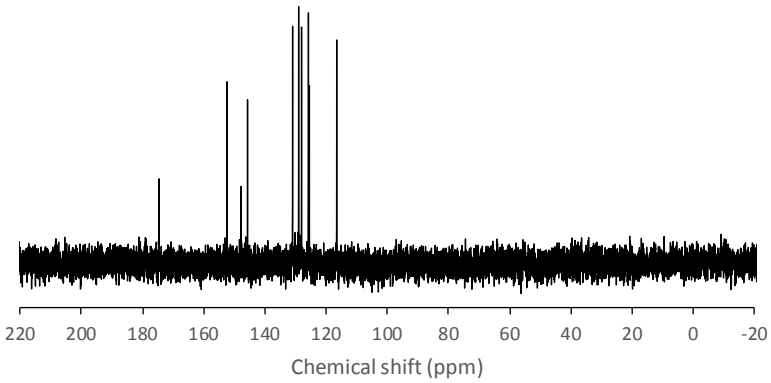

Figure S3. ^{13}C NMR spectrum of D_2O solution of **1** under air at room temperature.

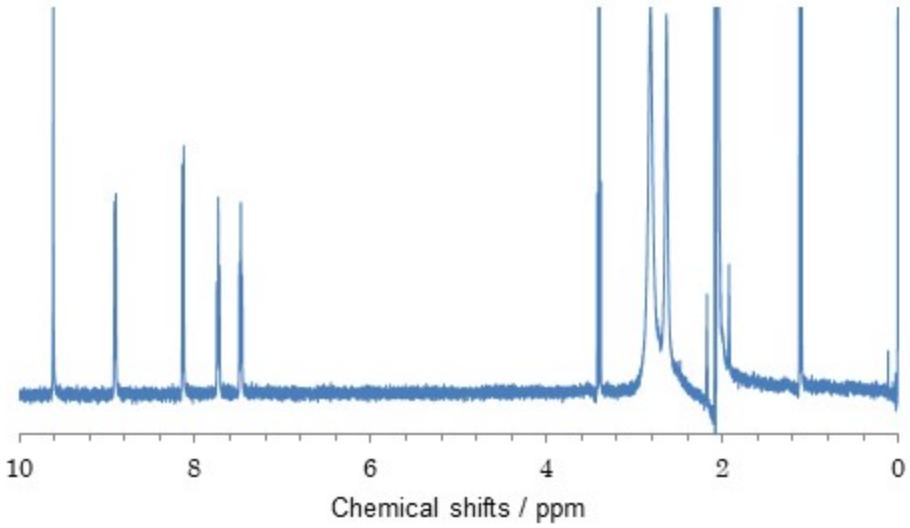

Figure S4. The ^{1}H NMR spectrum of acetone-d_6 solution of **3** at room temperature under air.

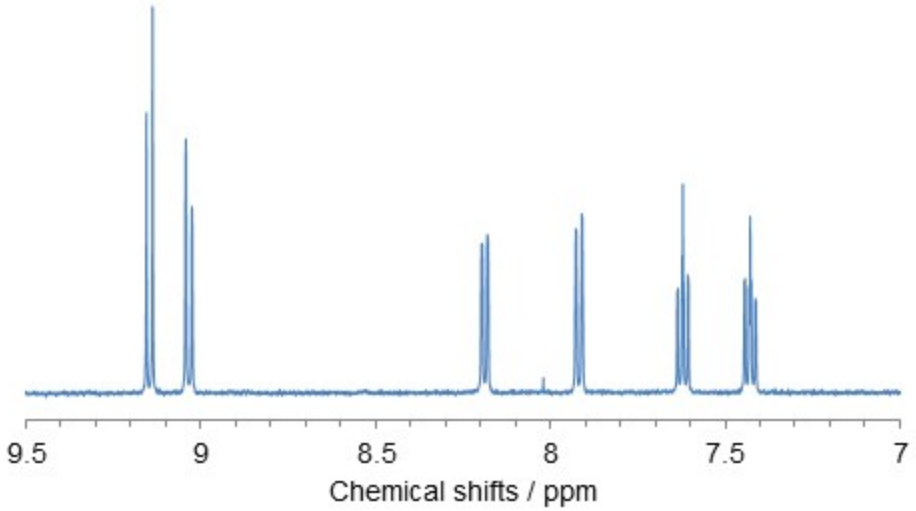

Figure S5 The ^{1}H NMR spectrum of acetone-d_6 solution of **4** at room temperature under air.

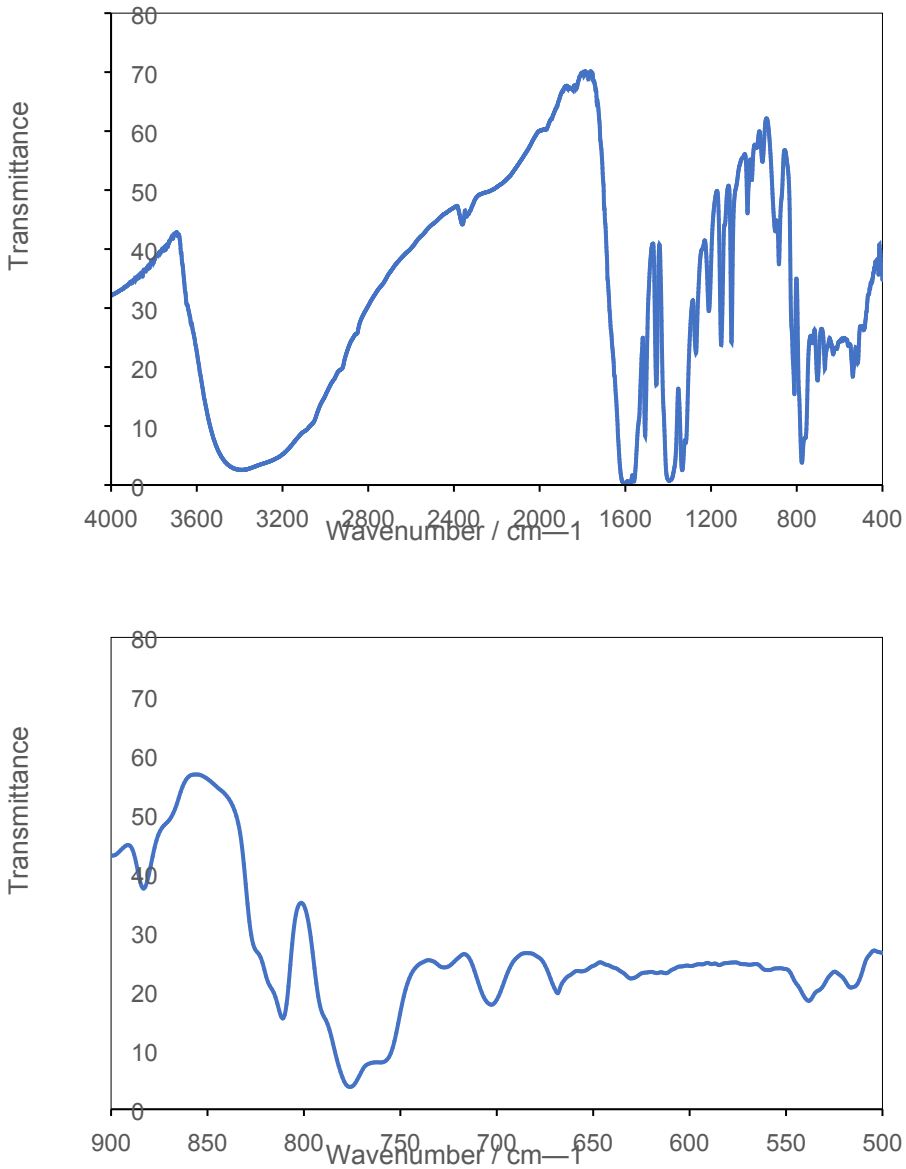

Figure S6. (top) The IR absorption spectrum of potassium bromide (KBr) pellet of the powder of **1** at room temperature under air. (bottom) Partial spectrum of the Figure.

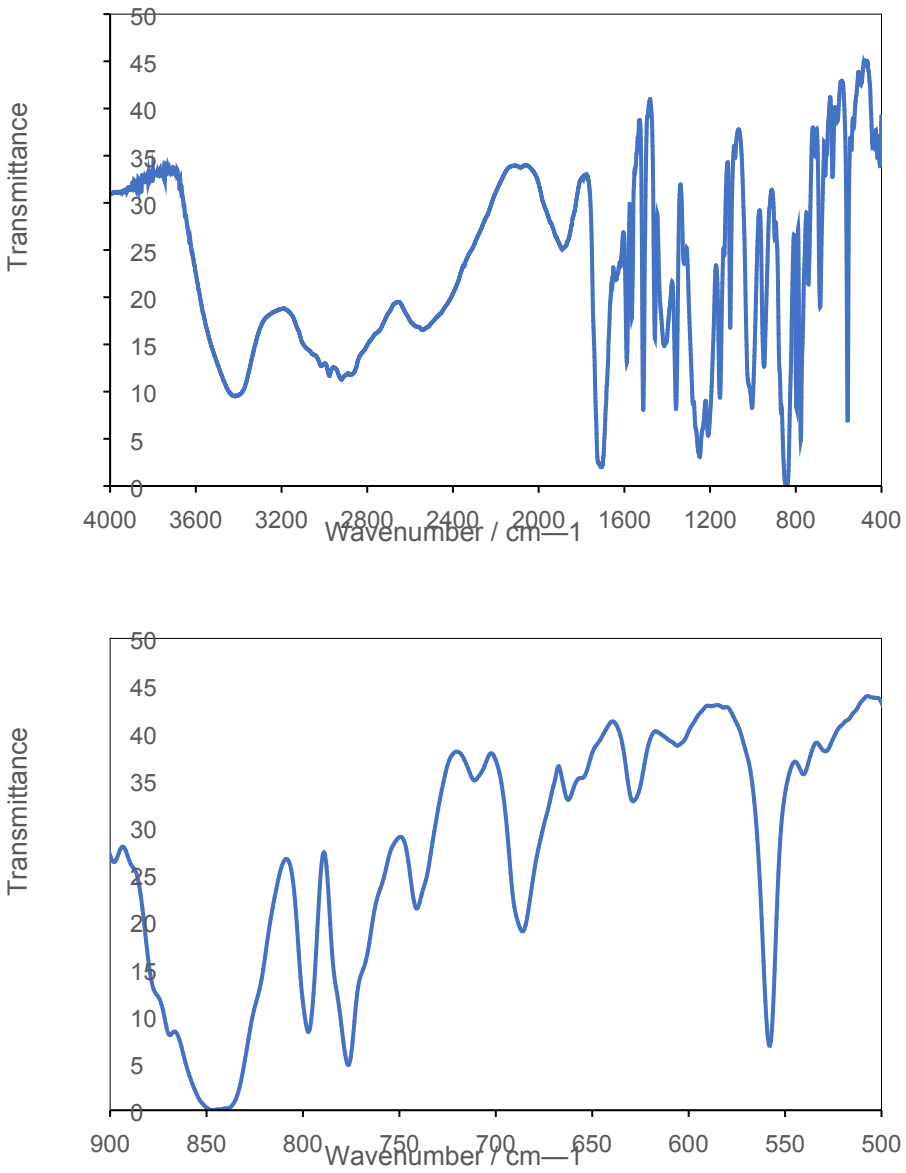

Figure S7. (top) The IR absorption spectrum of potassium bromide (KBr) pellet of the powder of **3** at room temperature under air. (bottom) Partial spectrum of the Figure.

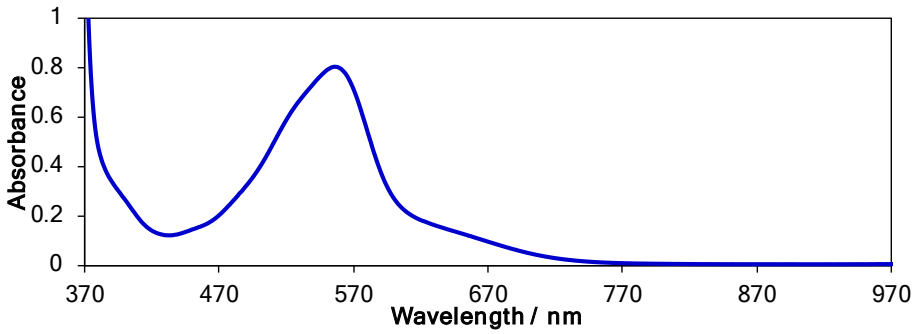

Figure S8. The transmission UV-vis absorption spectrum of **1** in ethanol at room temperature under air.

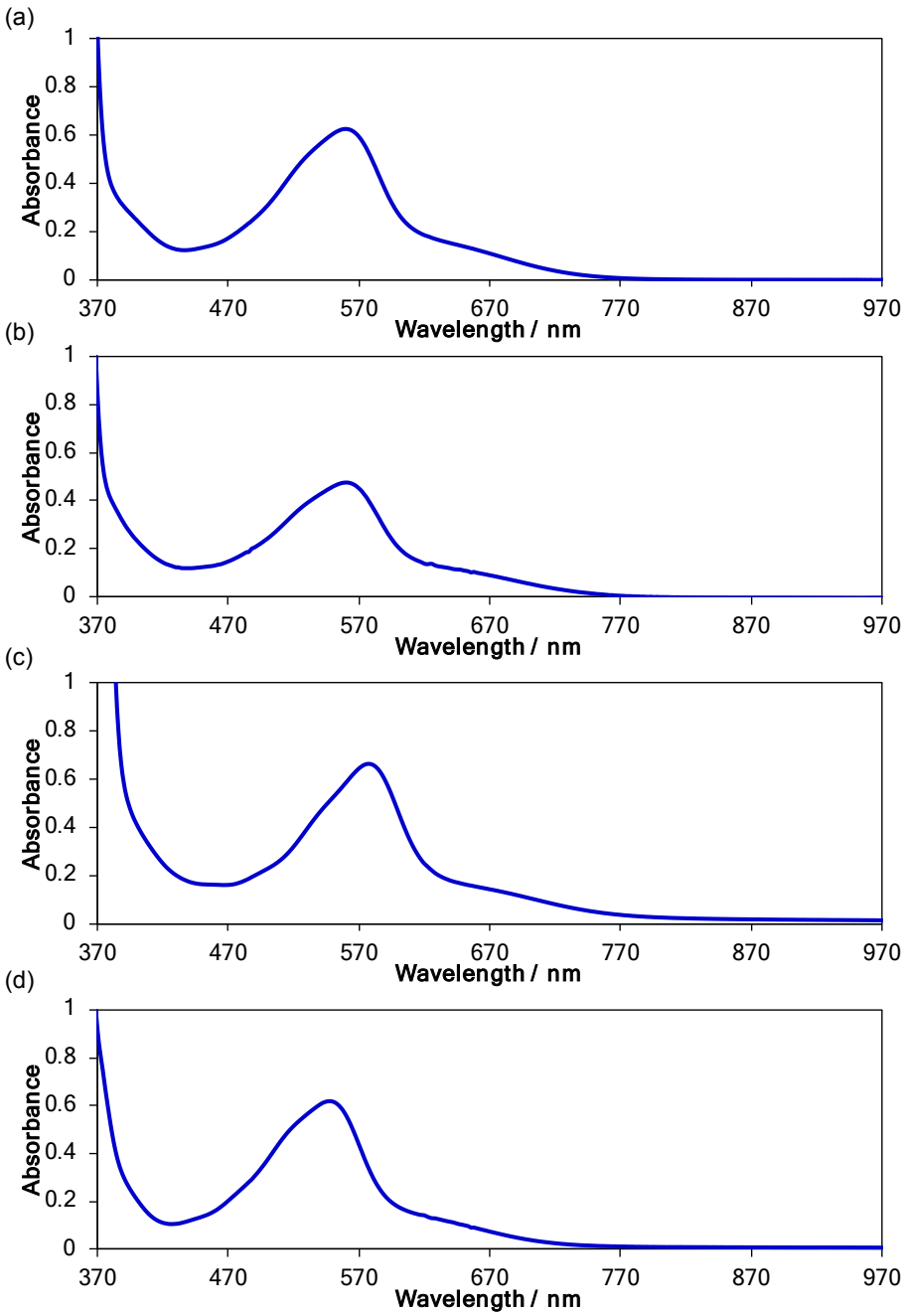

Figure S9. The transmission UV-vis absorption spectra of (a) **1** in water, (b) **2** in water, (c) **3** in acetone, and (d) **4** in acetone at room temperature under air.

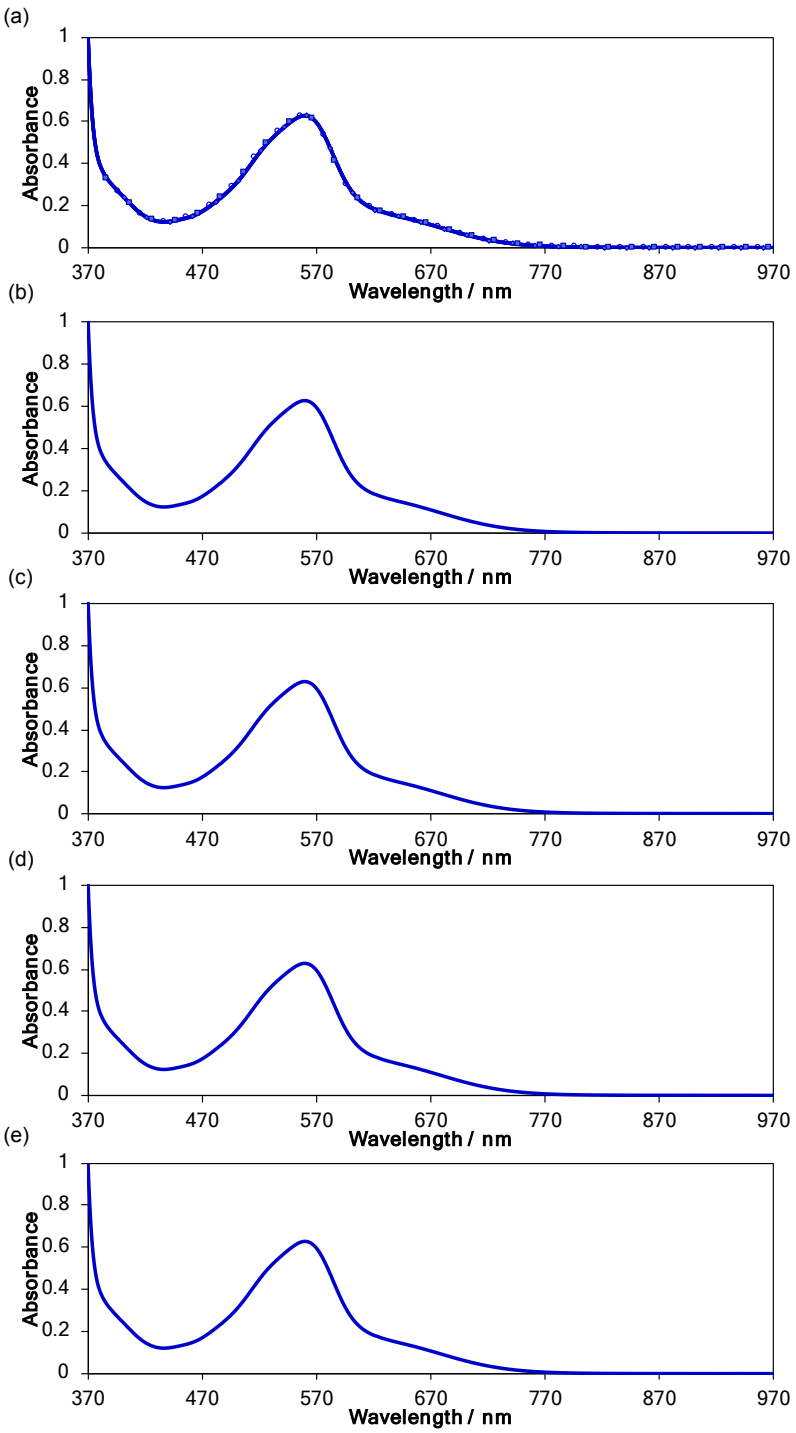

Figure S10. (a) Overlay of the time courses of the transmission UV-vis absorption spectra of **1** in water at room temperature under air measured after dissolving the powder as soon as possible (blue line with ■), after keeping of the same sample at room temperature under air after 60 min. (blue line with ○), 180 min. (blue line), and 1660 min. (blue line with ▲). The each four spectra are shown in (b), (c), (d), and (e).

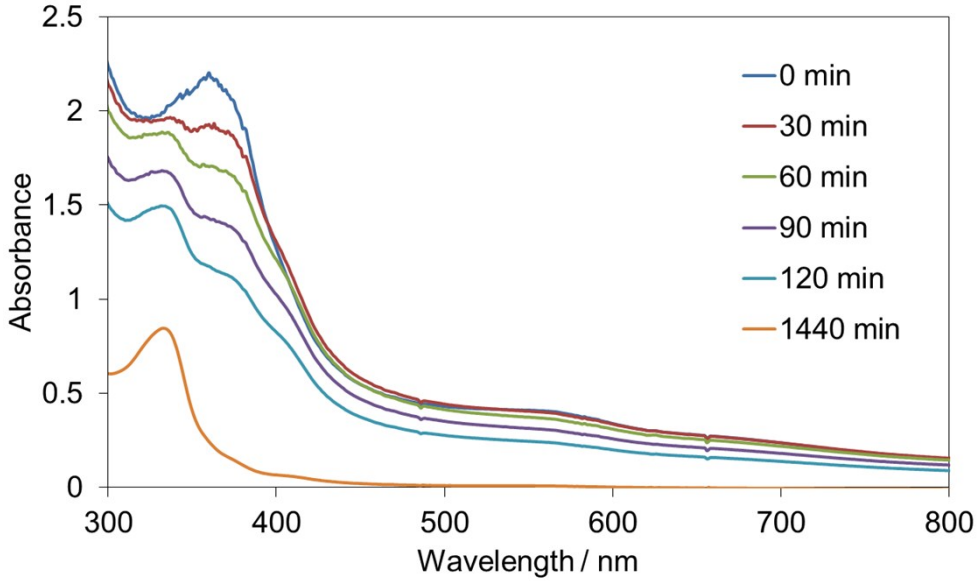

Figure S11. The time course of the transmission UV-vis absorption spectra of **1** in the presence of slight excess of $(NH_4)_2(Ce(NO_3)_6)$ in water at room temperature under air.

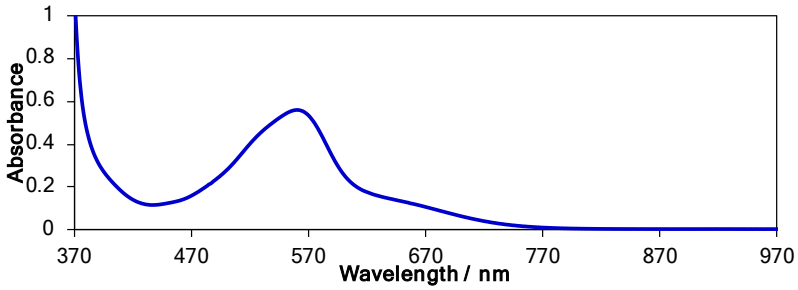

Figure S12. The transmission UV-vis absorption spectra of **1** in buffer solution using phthalate pH standard solution at room temperature under air.

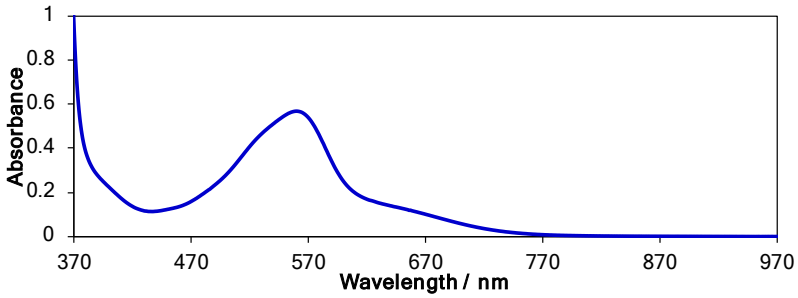

Figure S13. The transmission UV-vis absorption spectra of **1** in buffer solution using carbonate pH standard solution (pH 10.01) which consists of water (99 wt%), Na_2CO_3 (0.3 wt%), and $NaHCO_3$ at room temperature under air.

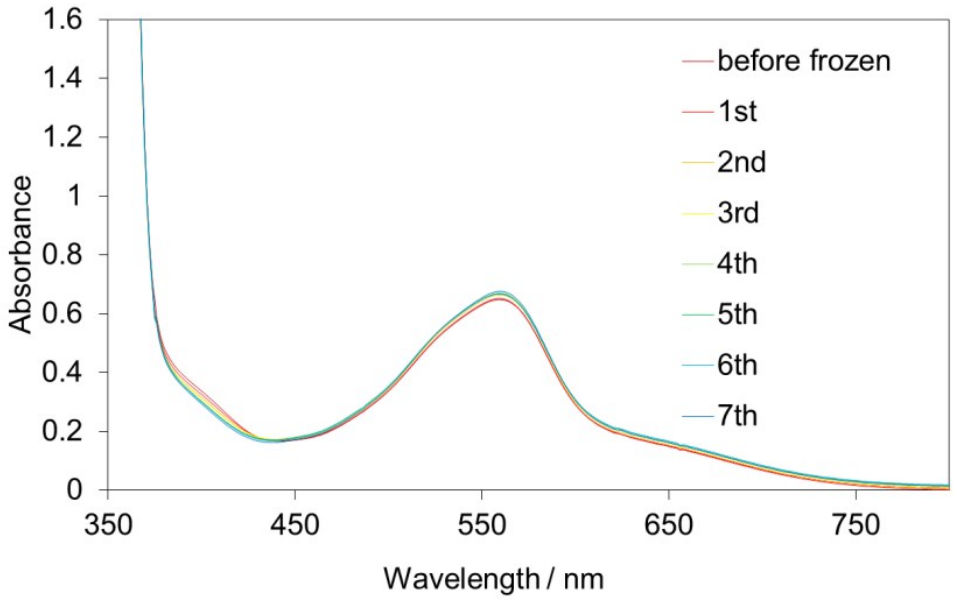

Figure S14. UV-vis transmission absorption spectra of **1** in water before freezing operation and after 1, 2, 3, 4, 5, 6, and 7 times operations of freezing operations followed by melting operations.

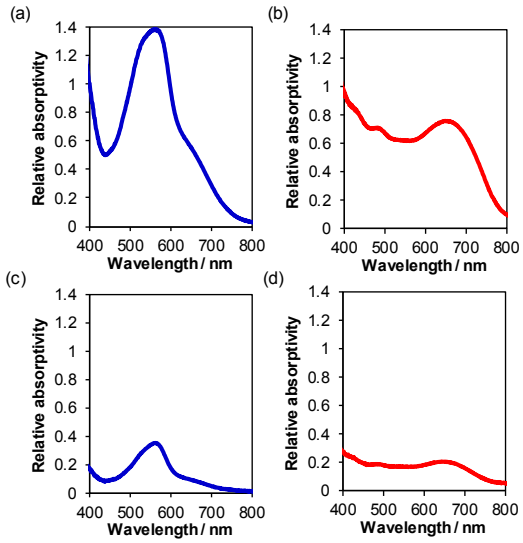

Figure S15. UV-vis spectra related to absorption using integrate sphere of **1** (1×10^{-3} M) in liquid water (a), frozen one (b), **1** (1×10^{-4} M) in liquid water (c), and frozen one (d).

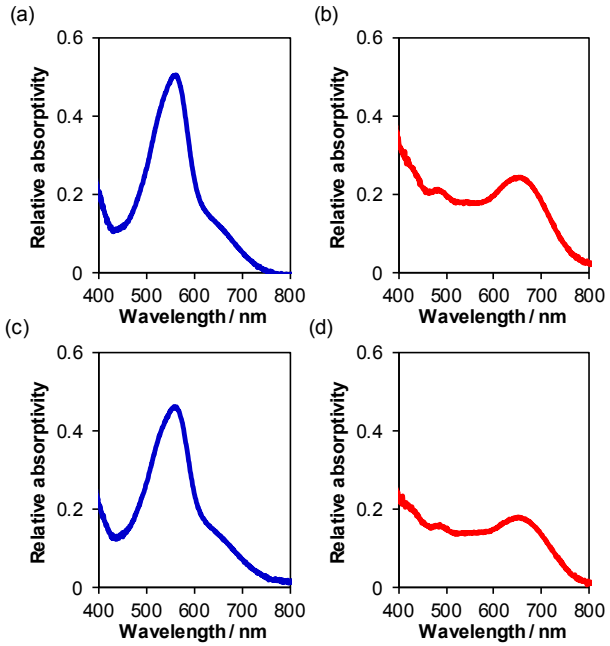

Figure S16. UV-vis spectra related to absorption using integrate sphere of **1** in carbonate pH standard solution (pH 10.01) which consists of water (99 wt%), Na_2CO_3 (0.3 wt%), and $NaHCO_3$ (a), frozen one (b), in tetraborate pH standard solution (pH = 9.18) which consists of water and sodium tetraborate decahydrate (c), and frozen one (d).