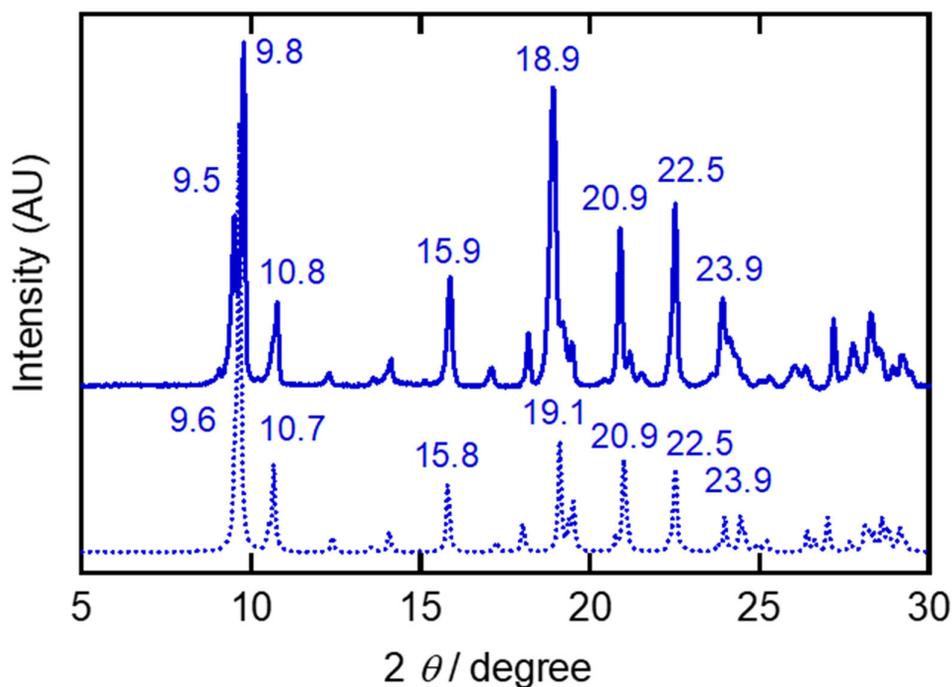
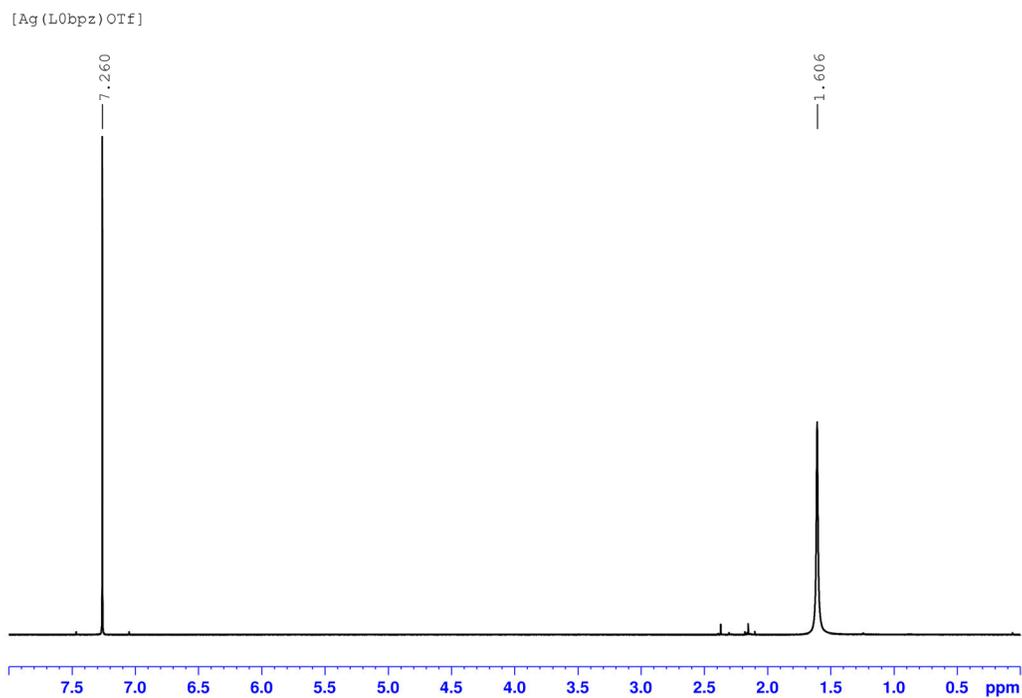


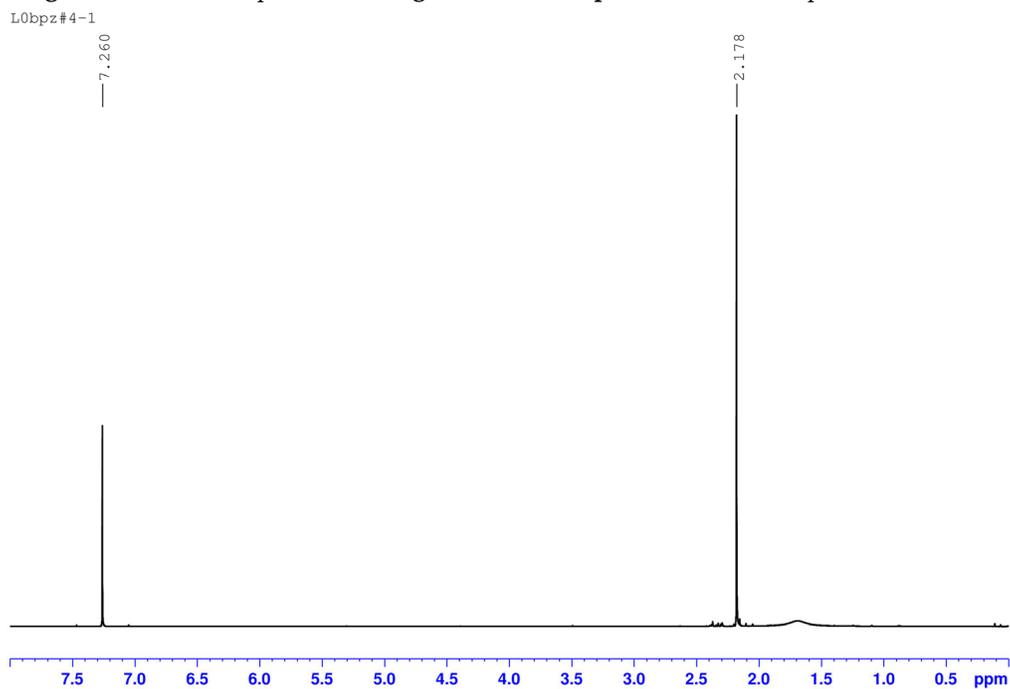
**Figure S1.** Powder X-ray diffractogram of  $[\text{Ag}(\text{CF}_3\text{CO}_2)(\text{Me}_1\text{bpzH}_2)]$  at room temperature. The simulated diffractogram (dashed line) is based on the X-ray data collected at  $-95\text{ }^\circ\text{C}$ .



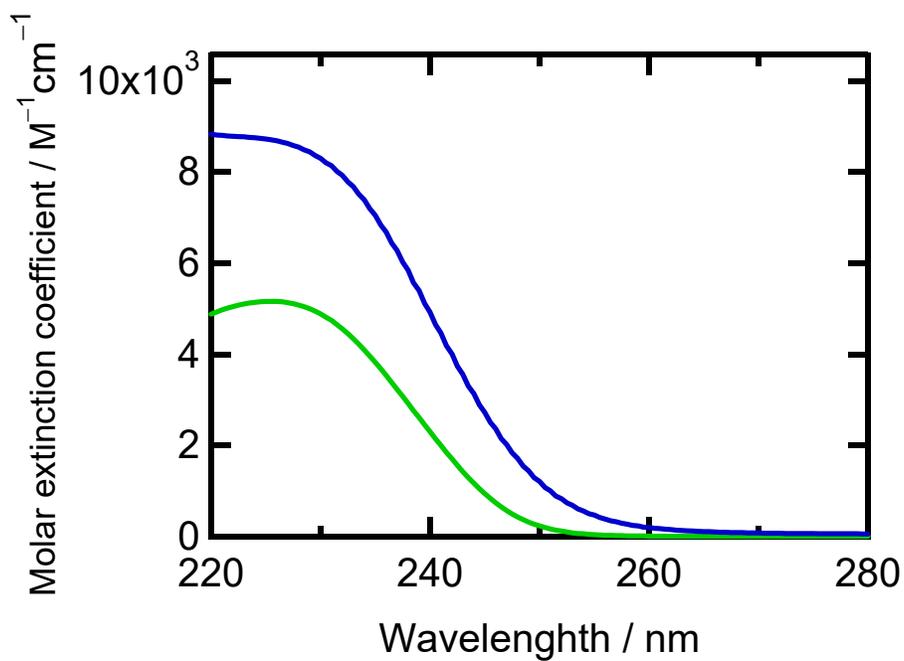
**Figure S2.** Powder X-ray diffractogram of  $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{Me}_1\text{bpzH}_2)]$  at room temperature. The simulated diffractogram (dashed line) is based on the X-ray data collected at  $-95\text{ }^\circ\text{C}$ .



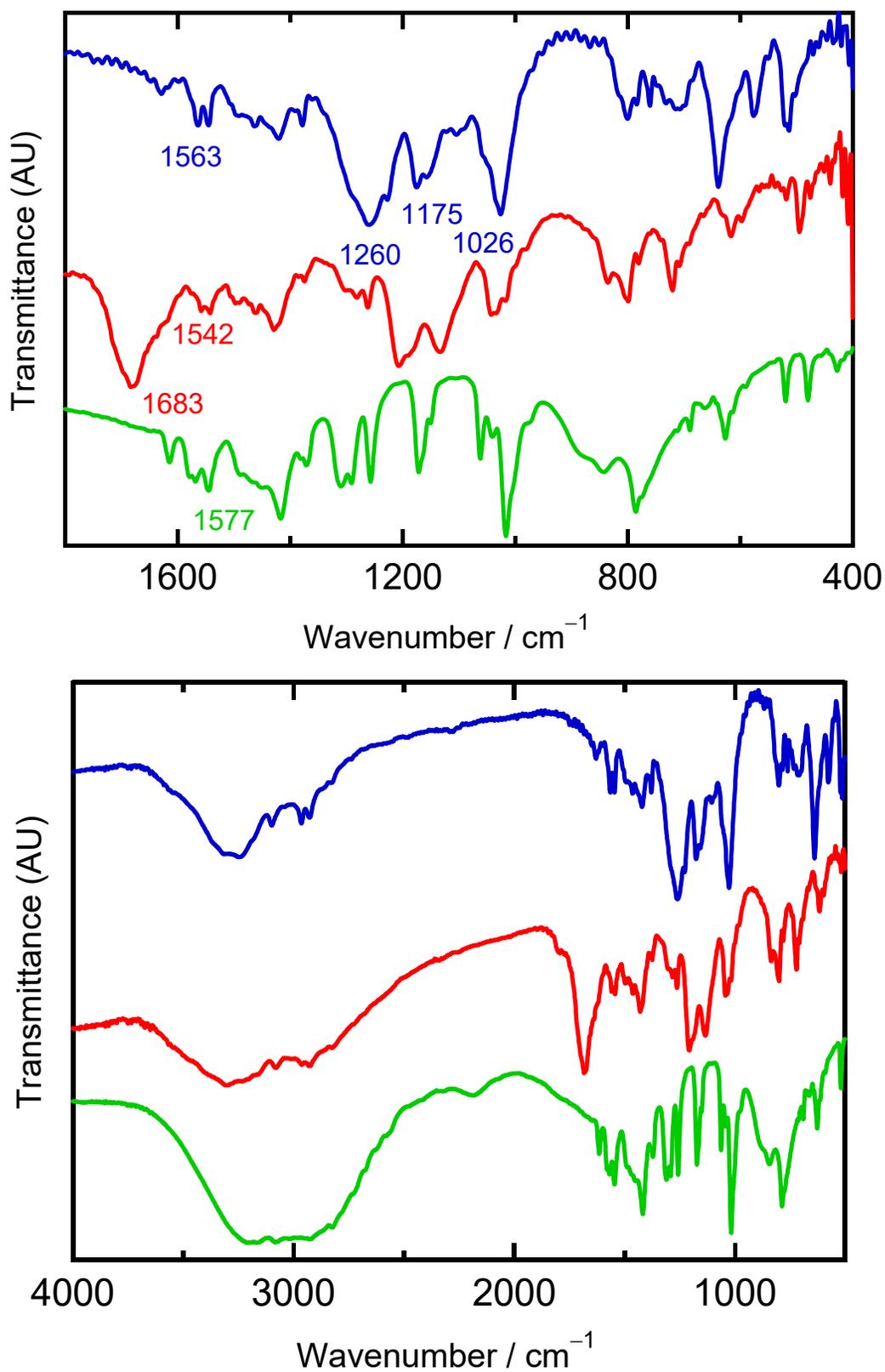
**Figure S3.**  $^1\text{H-NMR}$  spectrum of  $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{Me}_4\text{bpzH}_2)]$  at room temperature in  $\text{CDCl}_3$ .



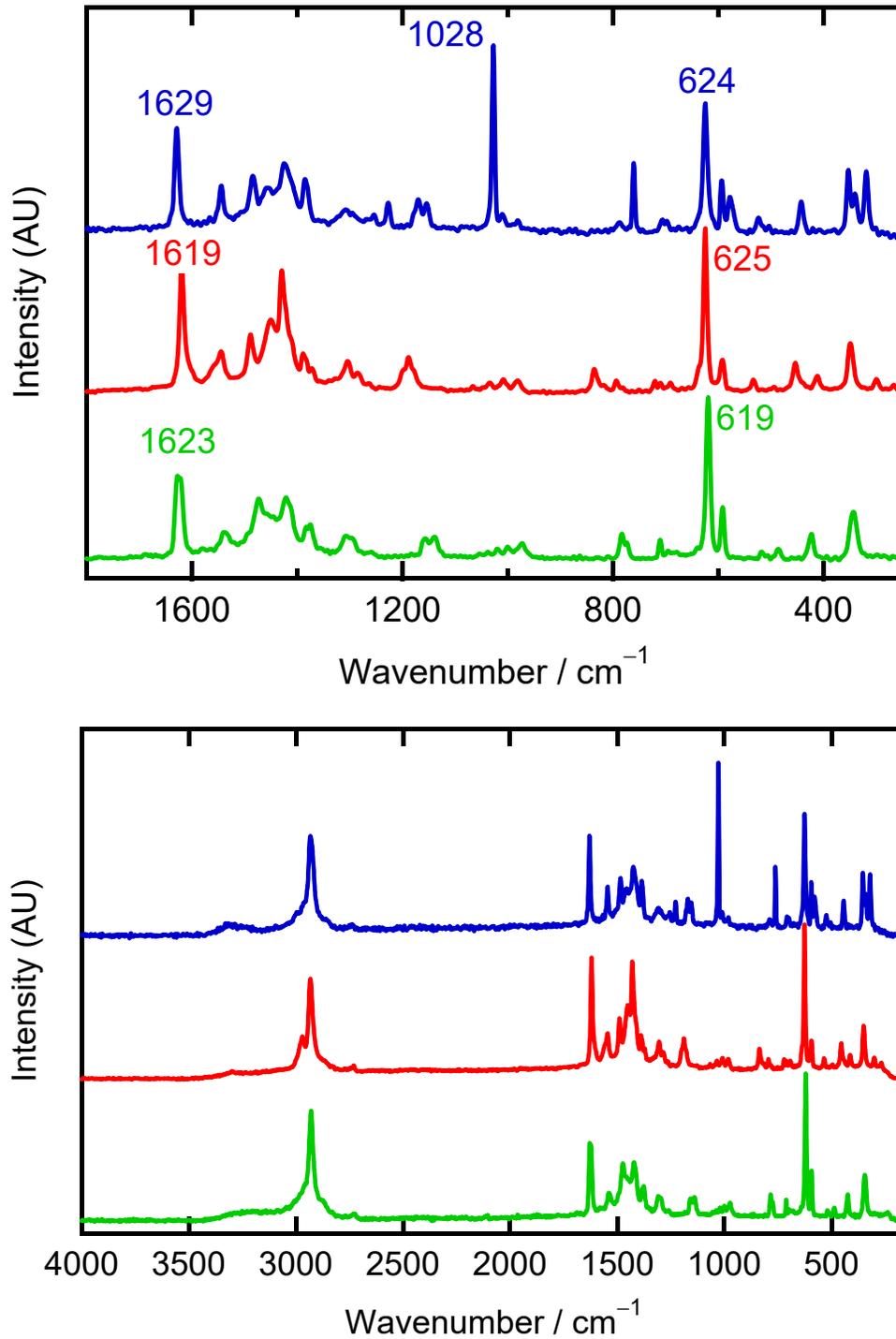
**Figure S4.**  $^1\text{H-NMR}$  spectrum of  $\text{Me}_4\text{bpzH}_2$  at room temperature in  $\text{CDCl}_3$ .



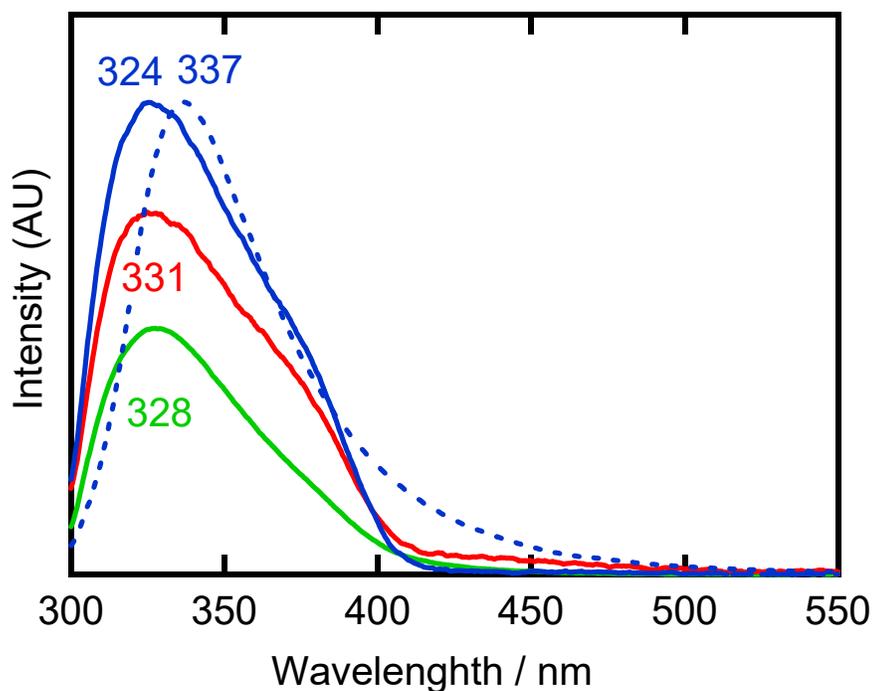
**Figure S5.** UV spectra of the ligand Me<sub>4</sub>bpzH<sub>2</sub> (green line) and silver(I) coordination polymers [Ag(CF<sub>3</sub>SO<sub>3</sub>)(Me<sub>4</sub>bpzH<sub>2</sub>)] (blue line) at room temperature in MeOH.



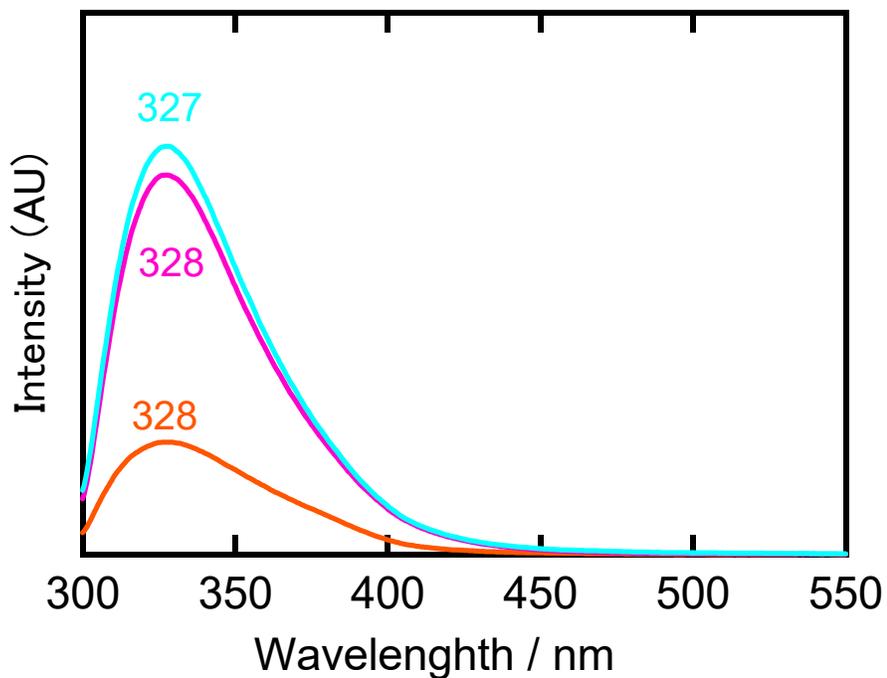
**Figure S6.** IR spectra of the ligand Me<sub>1</sub>bpzH<sub>2</sub> (green line) and silver(I) complexes [Ag(CF<sub>3</sub>CO<sub>2</sub>)(Me<sub>1</sub>bpzH<sub>2</sub>)] (red line) and [Ag(CF<sub>3</sub>SO<sub>3</sub>)(Me<sub>1</sub>bpzH<sub>2</sub>)] (blue line) at room temperature. Top: 4000–500 cm<sup>-1</sup> range, bottom: 1800–400 cm<sup>-1</sup> region.



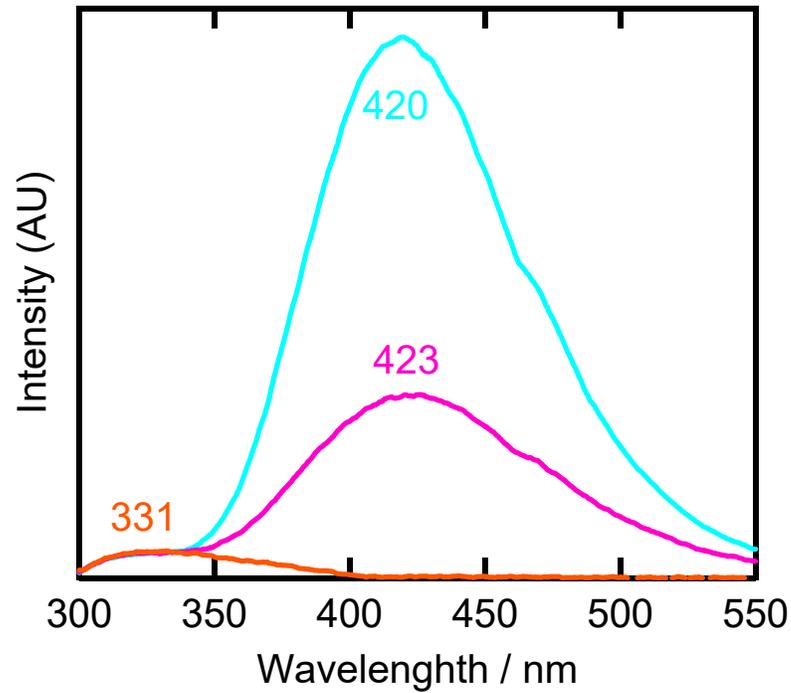
**Figure S7.** FT-Raman spectra (600 mW Laser power) of the ligand MeabpzH<sub>2</sub> (green line) and silver(I) complexes [Ag(CF<sub>3</sub>CO<sub>2</sub>)(MeabpzH<sub>2</sub>)] (red line) and [Ag(CF<sub>3</sub>SO<sub>3</sub>)(MeabpzH<sub>2</sub>)] (blue line) at room temperature. Top: 4000–150 cm<sup>-1</sup> range, bottom: 1800–250 cm<sup>-1</sup> region.



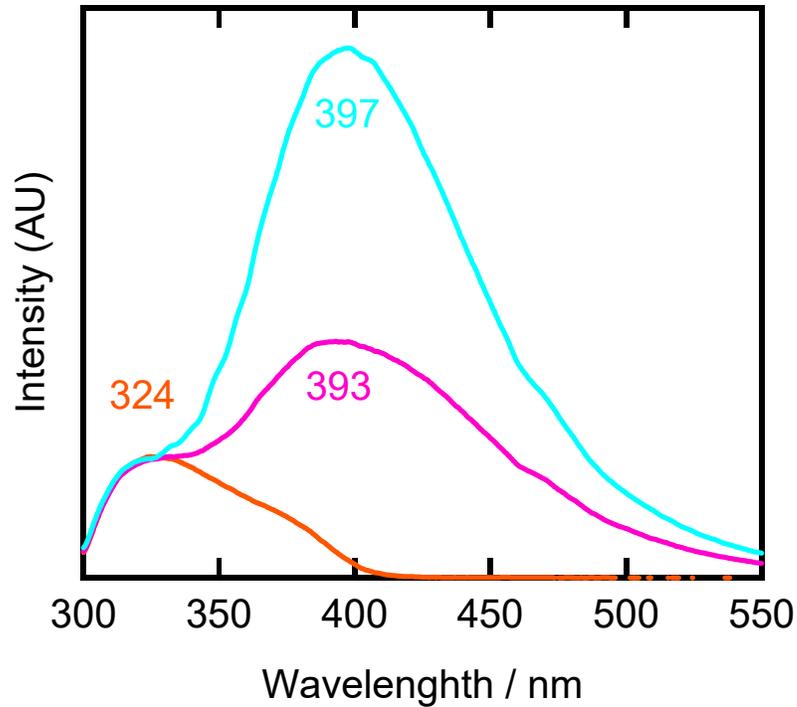
**Figure S8.** Photoluminescence spectra of the ligand  $\text{Me}_4\text{bpzH}_2$  (solid-state, green line at 250 nm excitation), and silver(I) complexes  $[\text{Ag}(\text{CF}_3\text{CO}_2)(\text{Me}_4\text{bpzH}_2)]$  (solid-state, red line at 250 nm excitation) and  $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{Me}_4\text{bpzH}_2)]$  (solid-state, blue line at 240 nm excitation and solution-state in MeOH, blue dashed line at 260 nm excitation) at 298 K.



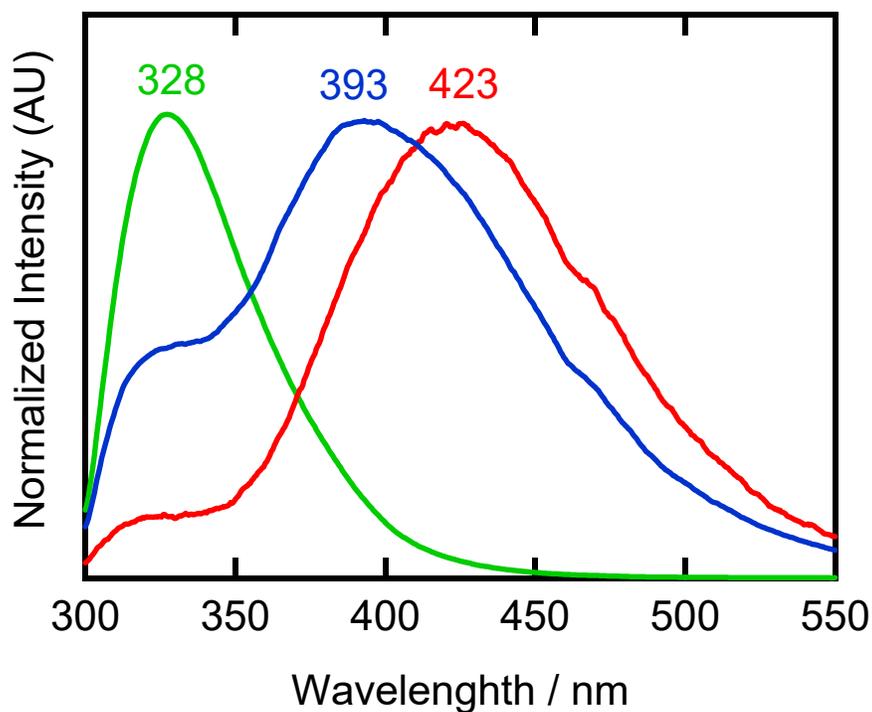
**Figure S9.** Temperature dependent photoluminescence spectra of the ligand  $\text{Me}_4\text{bpzH}_2$  (solid-state) at 250 nm excitation wavelength, temperatures: 83 K (light blue), 173 K (purple), and 298 K (orange).



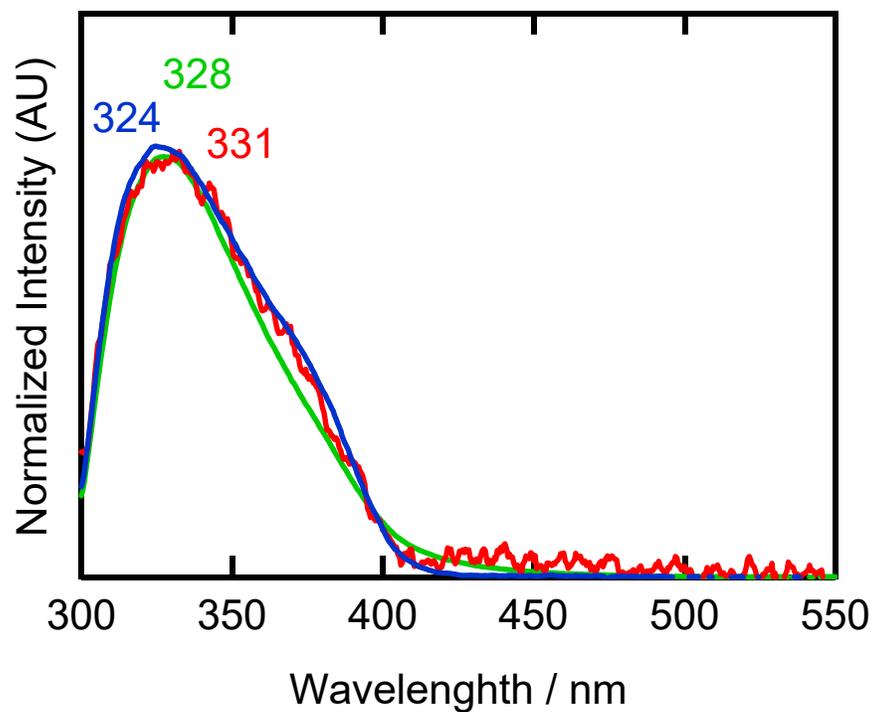
**Figure S10.** Temperature dependent photoluminescence spectra of  $[\text{Ag}(\text{CF}_3\text{CO}_2)(\text{Me}_4\text{bpzH}_2)]$  (solid-state) at 250 nm excitation wavelength, (83 K (light blue), 173 K (purple), and 298 K (orange)).



**Figure S11.** Temperature dependent photoluminescence spectra of  $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{Me}_4\text{bpzH}_2)]$  (solid-state) at 240 nm excitation wavelength, (83 K (light blue), 173 K (purple), and 298 K (orange)).



**Figure S12.** Solid-state photoluminescence spectra of the ligand Me<sub>4</sub>bpzH<sub>2</sub> (green line, 250 nm excitation) and silver(I) complexes [Ag(CF<sub>3</sub>CO<sub>2</sub>)(Me<sub>4</sub>bpzH<sub>2</sub>)] (red line, 250 nm excitation) and [Ag(CF<sub>3</sub>SO<sub>3</sub>)(Me<sub>4</sub>bpzH<sub>2</sub>)] (blue line, 240 nm excitation) at 173 K



**Figure S13.** Solid-state photoluminescence spectra of the ligand Me<sub>4</sub>bpzH<sub>2</sub> (green line, 250 nm excitation) and silver(I) complexes [Ag(CF<sub>3</sub>CO<sub>2</sub>)(Me<sub>4</sub>bpzH<sub>2</sub>)] (red line, 250 nm excitation) and [Ag(CF<sub>3</sub>SO<sub>3</sub>)(Me<sub>4</sub>bpzH<sub>2</sub>)] (blue line, 240 nm excitation) at 298 K.