

# A Stable 1D Helical Silver Coordination Polymer with Red Emission

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## Experimental section

**Materials and Physical Measurements.** Commercially available chemicals were purchased and used without further purification. Powder X-ray diffraction (PXRD) measurement was performed on a TTRIII X-ray diffractometer (Rigaku, Japan) with Cu K $\alpha$  radiation at 40 kV and 200 mA. FTIR spectra were recorded in the range 4000–400 cm<sup>-1</sup> on a Thermo Nicolet spectroscopy by using KBr pellets. Thermo gravimetric analysis (TGA) was performed on a NETZSCH STA 449F3 instrument with the heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Microscope image of the crystal was performed on OLYMPUS-DP80. X-ray single crystal diffraction measurement was performed on Bruker APEX-II CCD (Cu X-ray source). Fluorescent lifetime was measured on an Edinburgh FLS980 fluorescence spectrometer equipped. <sup>1</sup>H-NMR spectra were measured on a Bruker spectrometer (400 MHz) at 25 °C in CDCl<sub>3</sub>. All calculations were performed using the Gaussian 09 program. All the structures were completely optimized using a combined basis set: the LanL2DZ basis set was used for Ag along with the 6-31G(d) basis set for C, N, H, F, S, and O. To avoid complexity, we treated Ag-Bz as a truncated segment containing one Ag<sub>5</sub>(CF<sub>3</sub>COO)(Bz)(S<sup>t</sup>Bu)<sub>4</sub> unit.

**Synthesis of AgS<sup>t</sup>Bu.** AgS<sup>t</sup>Bu was prepared according to published protocols<sup>1</sup>.

**Synthesis of Ag-Bz.** AgS<sup>t</sup>Bu (0.1086 g, 0.55 mmol), CF<sub>3</sub>COOAg (0.0607 g, 0.28 mmol) and benzimidazole (0.0590 g, 0.5 mmol) were dissolved in a mixed solvent 1mL

of MeOH: DMF =1:1 under ultrasonic. The obtained solution was slowly evaporated in air at room temperature to give needle-like colorless crystals that were rinsed with EtOH, filtered and dried in air to produce Ag-Bz with a 55% yield based on silver element.

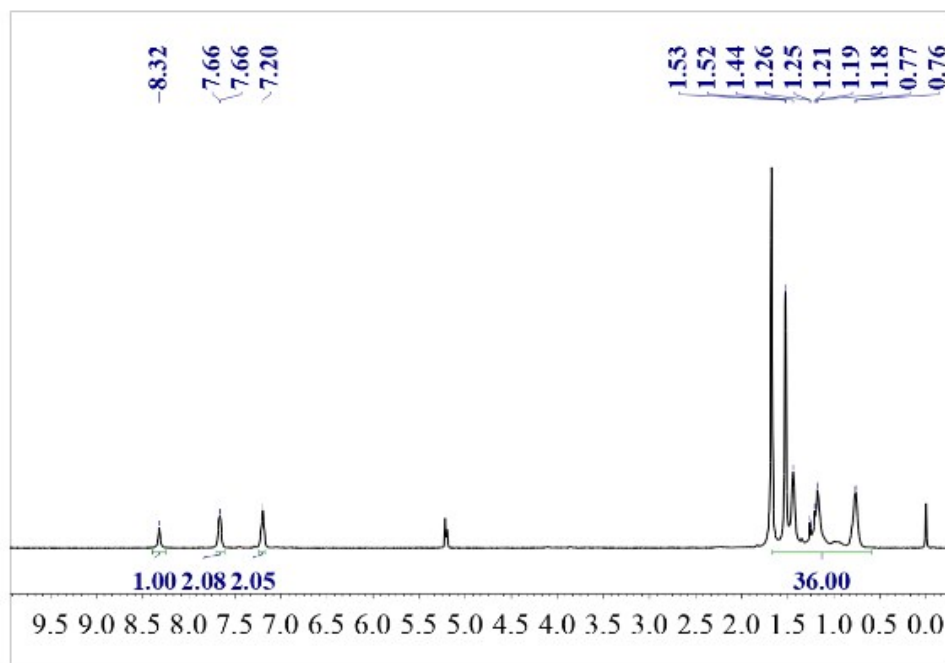
**Crystal Data Collection and Refinement.** The crystal data of Ag-Bz was collected on a Bruker APEX-III CCD diffractometer at room temperature using Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The structure was resolved and refined using the SHELX-97 software. Crystal data was listed in Table S1. Crystallographic data were deposited in the Cambridge Structural Date Centre (CCDC) and can be obtained free of charge at <http://www.ccdc.cam.ac.uk/> by using reference numbers 1859816.



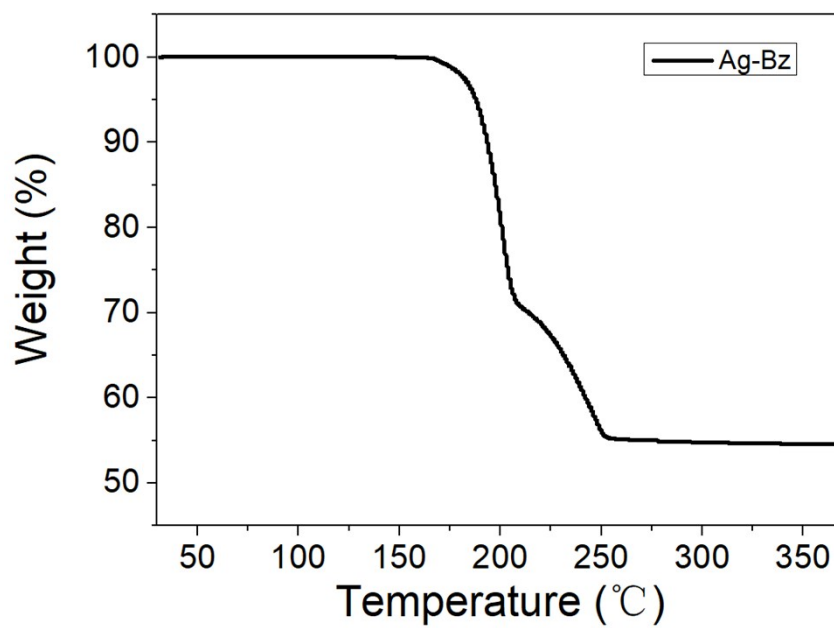
**Figure S1.** Microscope image of the crystal. (magnification is 20)



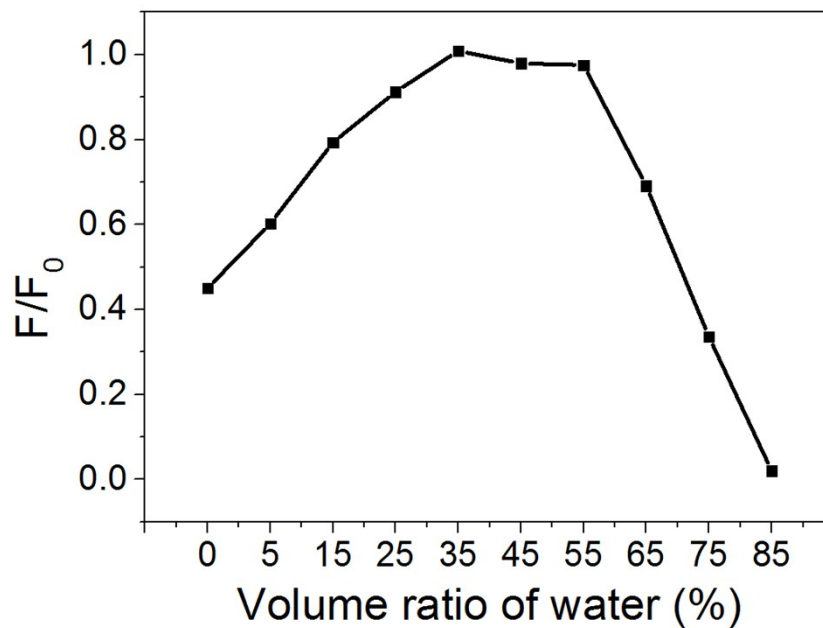
**Figure S2.** Microscope image of the crystal. (magnification is 60)



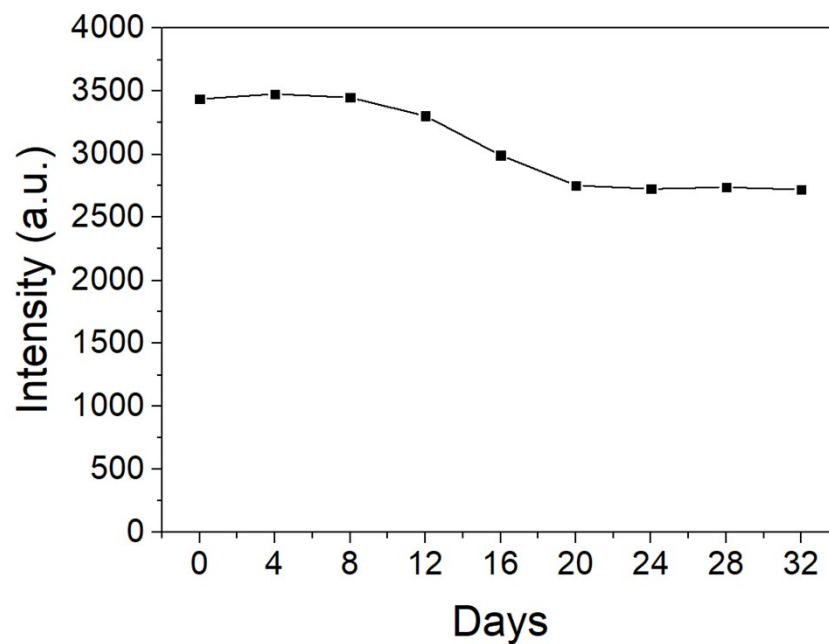
**Figure S3.**  $^1\text{H}$ NMR of Ag-Bz in  $\text{CDCl}_3$ .



**Figure S4.** TGA spectrum of Ag-Bz powder.



**Figure S5.** Plots of relative PL intensity of Ag-Bz at different water partial volume (excitation at 548 nm).



**Figure S6.** The stability of fluorescent intensity of Ag-Bz.

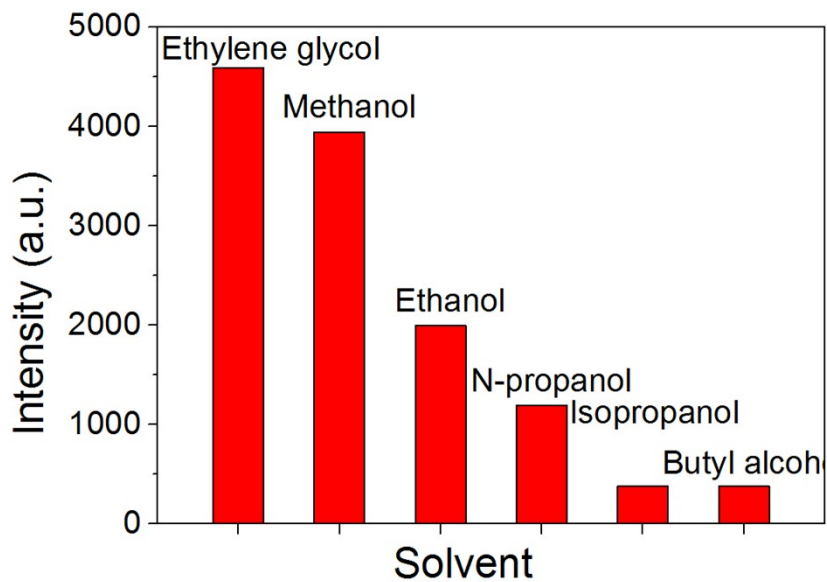


Figure S7. Fluorescent intensity of Ag-Bz in different solutions.

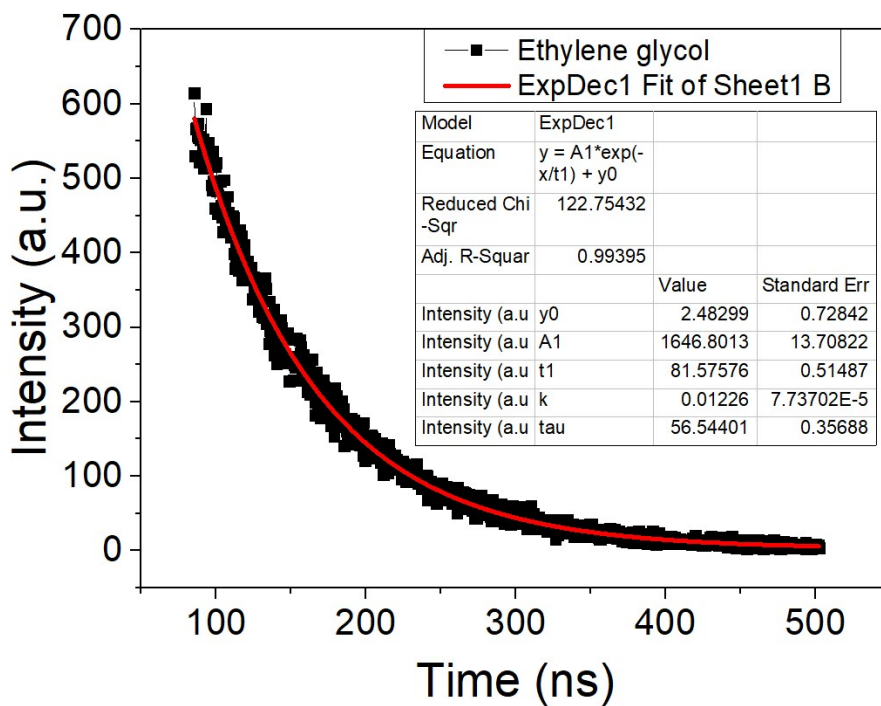
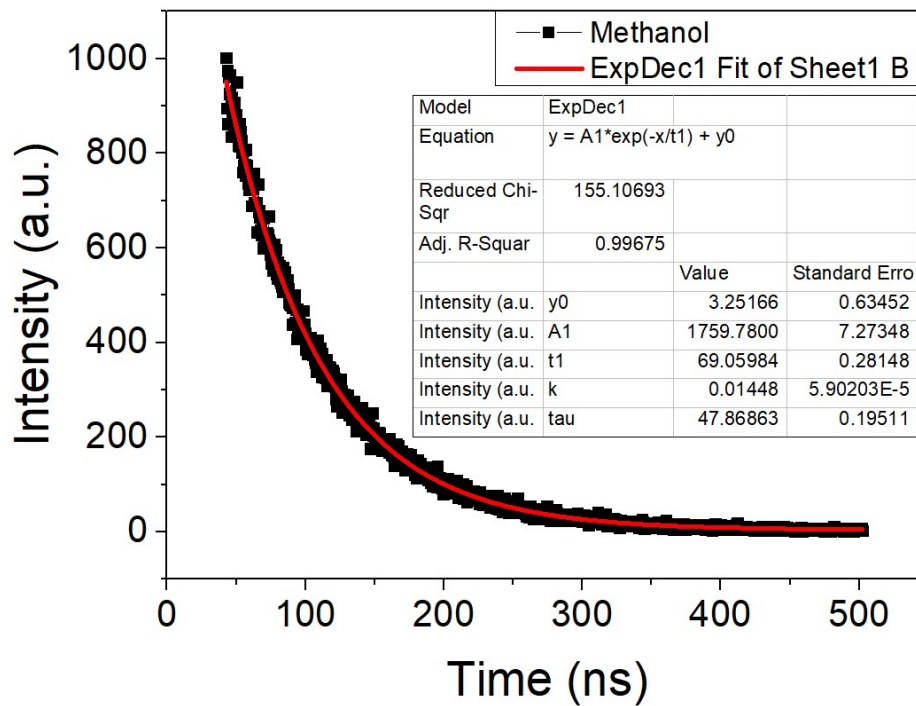
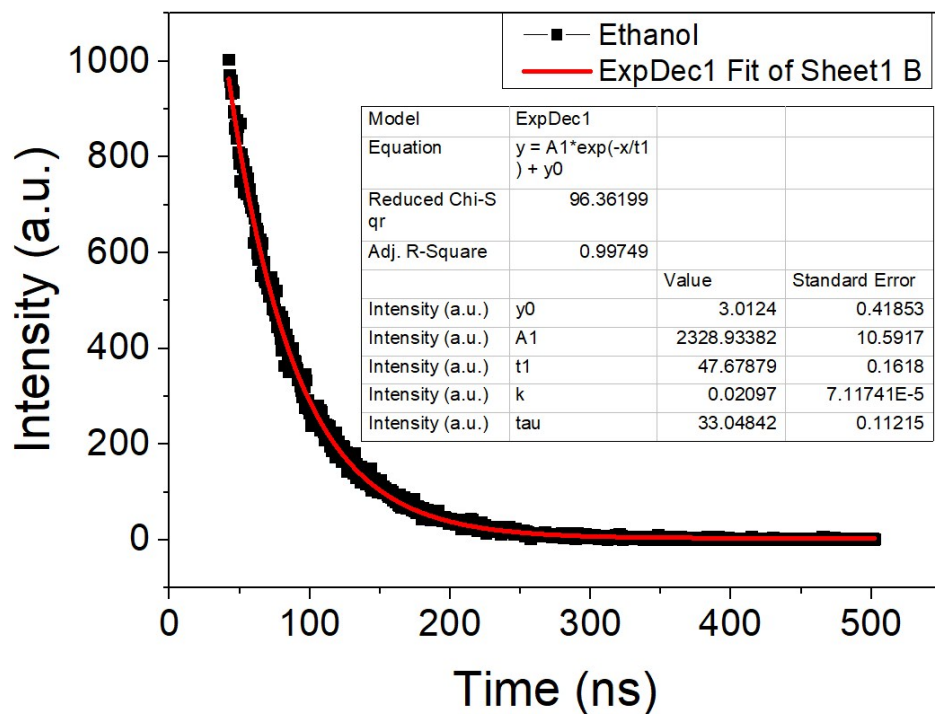


Figure S8. Fluorescent lifetime of Ag-Bz in ethylene glycol.



**Figure S9.** Fluorescent lifetime of Ag-Bz in methanol.



**Figure S10.** Fluorescent lifetime of Ag-Bz in ethanol.



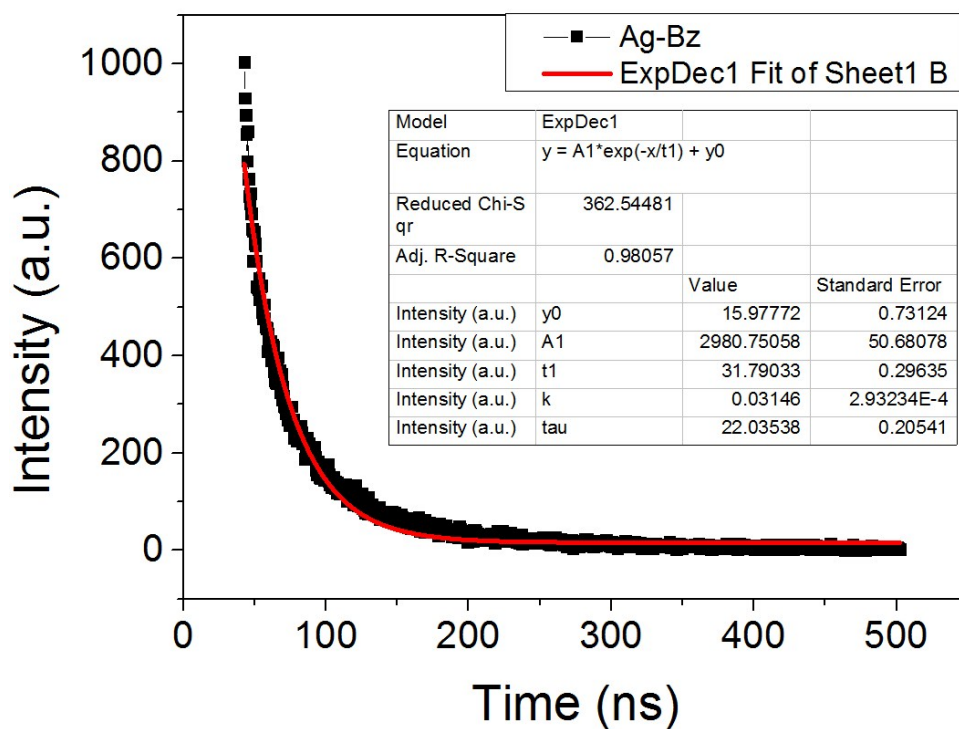


Figure S11. Fluorescent lifetime of Ag-Bz in solid state.

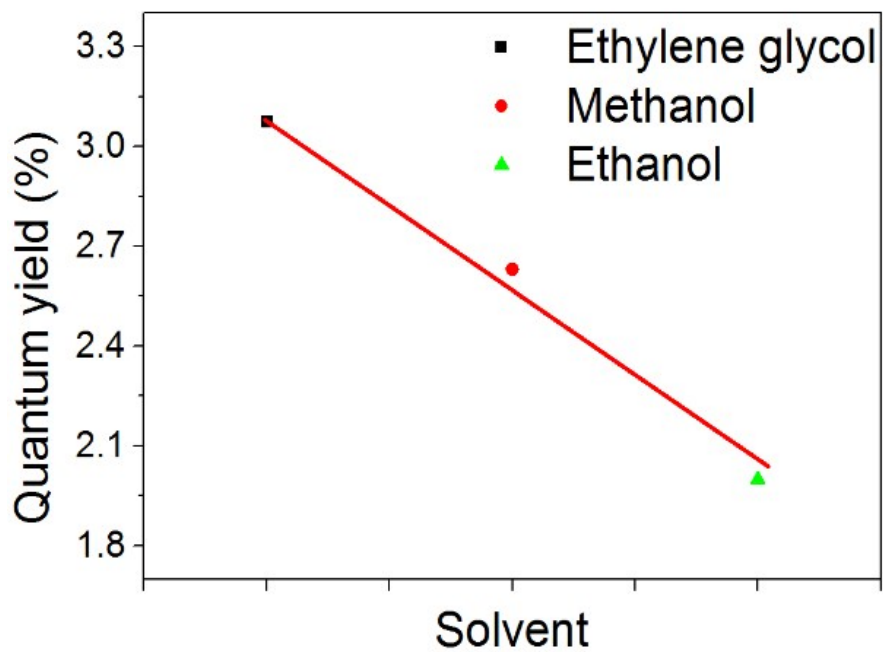
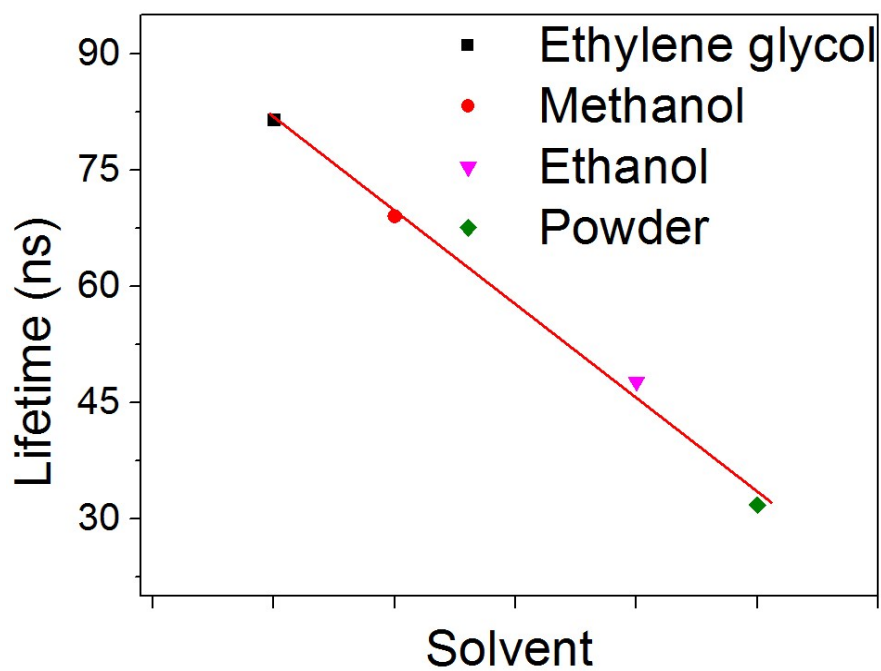
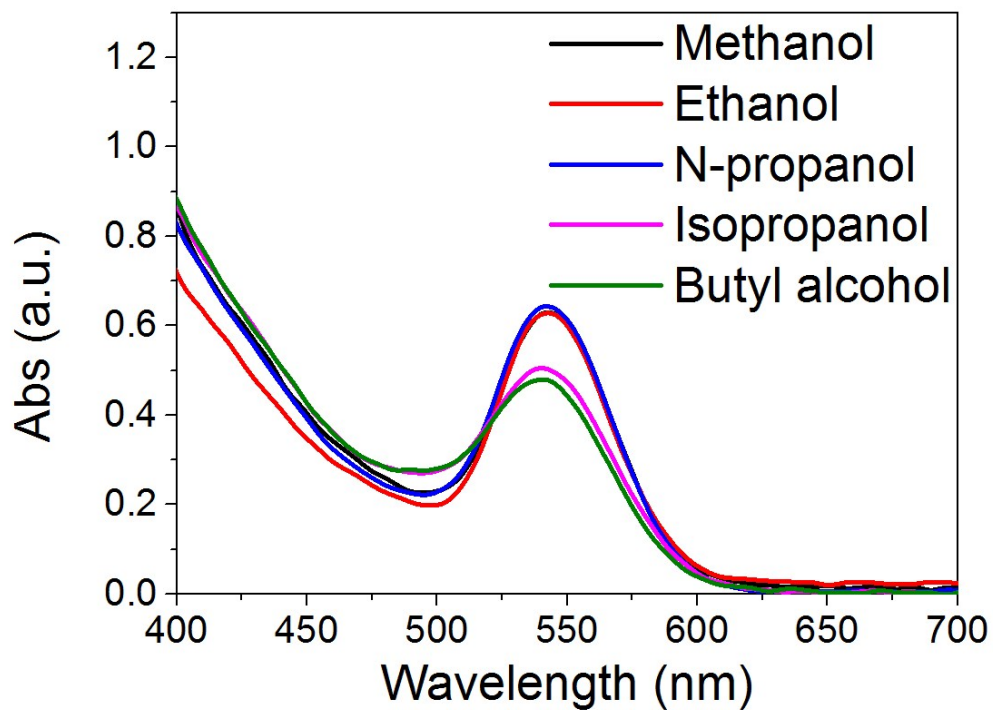


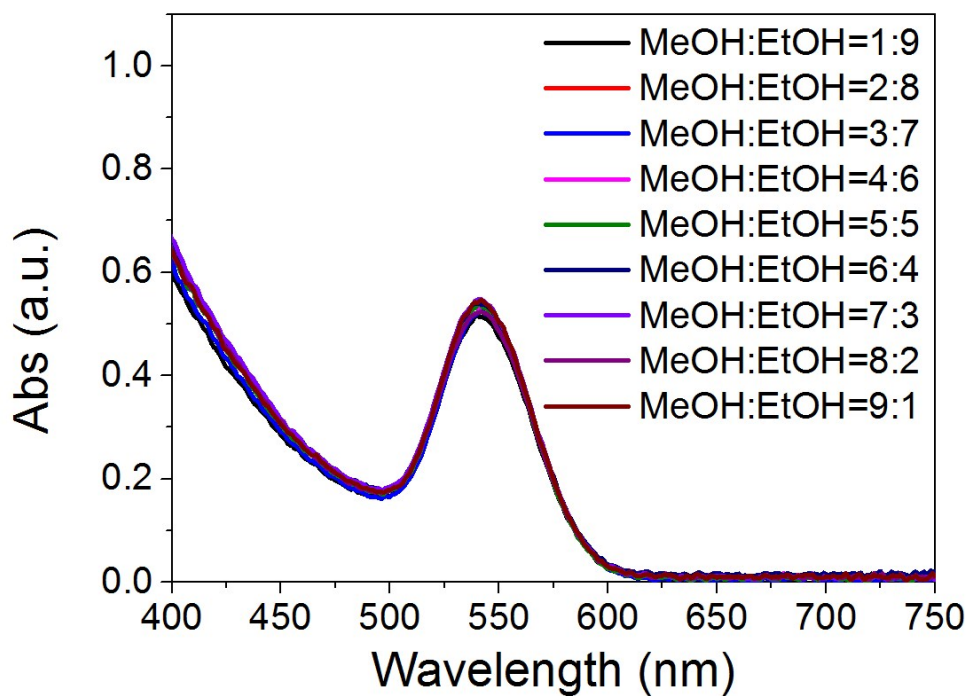
Figure S12. Fluorescence quantum yield of Ag-Bz in different solution.



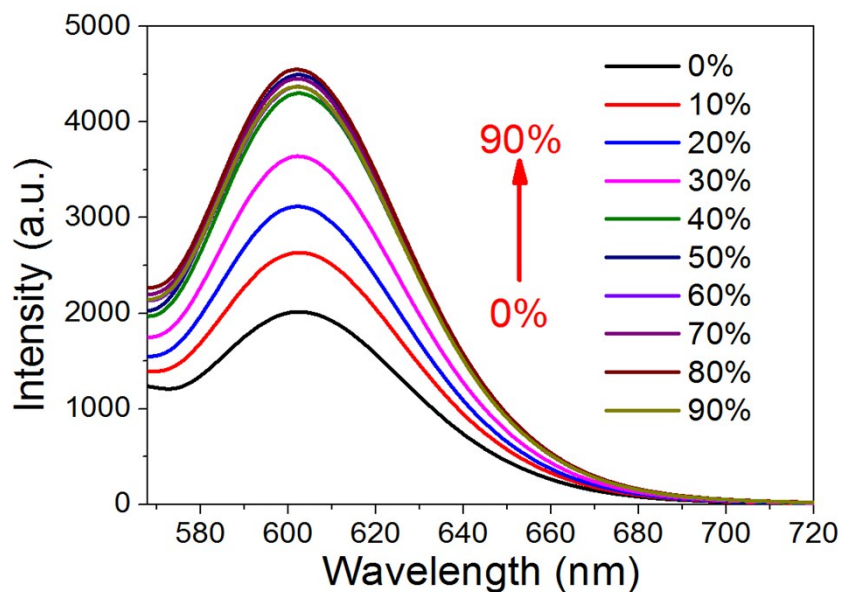
**Figure S13.** Fluorescent lifetime of Ag-Bz in different solvent.



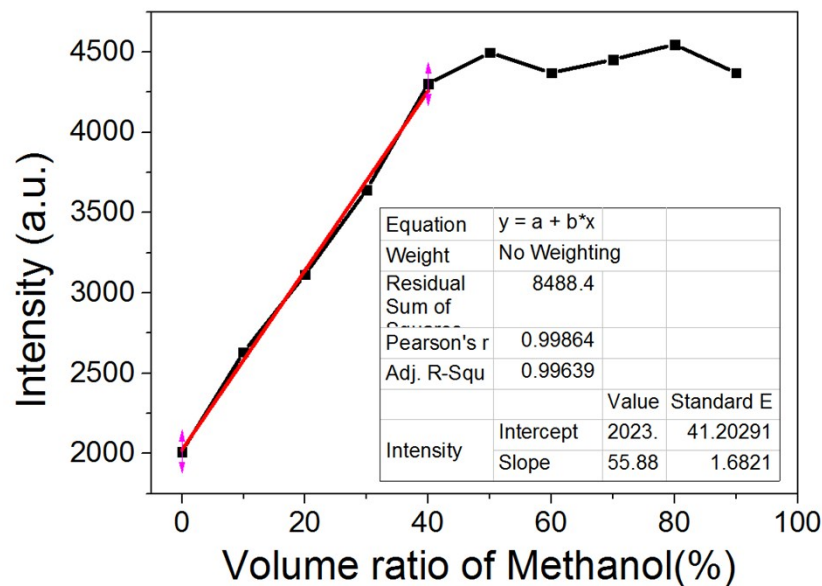
**Figure S14.** UV/Vis absorption of Ag-Bz indifferent alcohol solution.



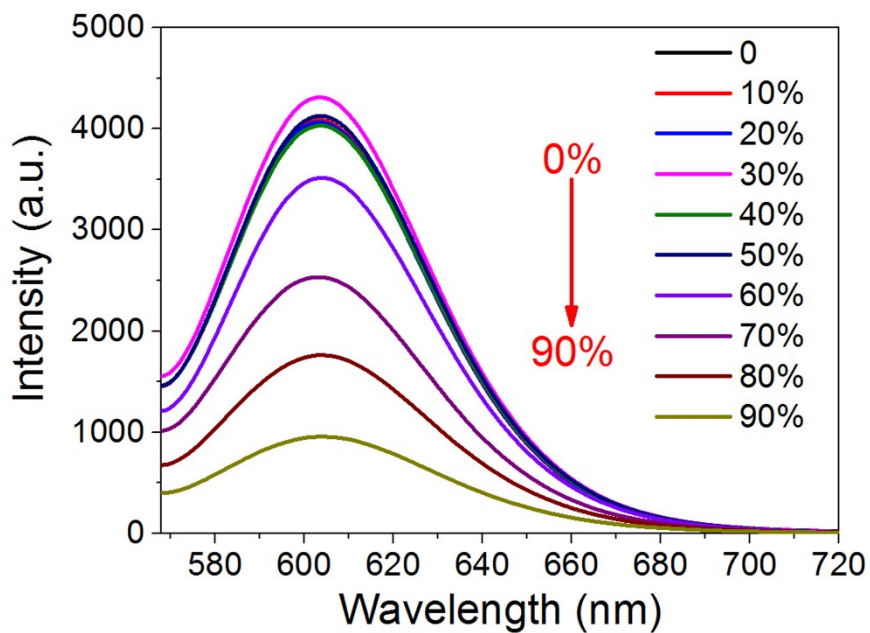
**Figure S15.** UV/Vis absorption of Ag-Bz in MeOH/EtOH mixed solution.



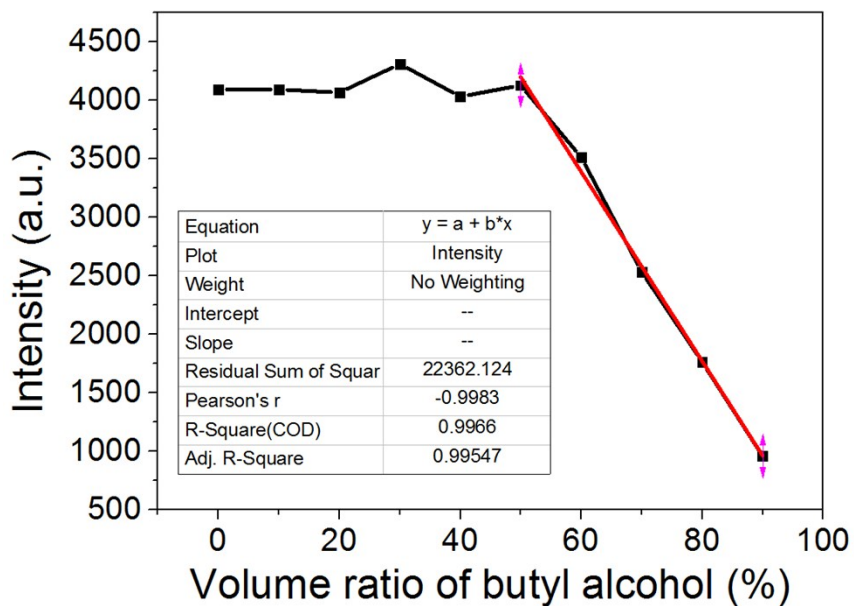
**Figure S16.** Fluorescent emission spectra of Ag-Bz at different MeOH partial volume (excitation at 548 nm) in the EtOH mixture.



**Figure S17.** Plots of relative PL intensity of Ag-Bz at different MeOH partial volume (excitation at 548 nm) in the EtOH mixture.



**Figure S18.** Emission spectra of Ag-Bz at different butyl alcohol partial volume (excitation at 548 nm) in the MeOH mixture.



**Figure S19.** Emission spectra and Plots of relative PL intensity of Ag-Bz at different butyl alcohol partial volume (excitation at 548 nm) in the MeOH mixture.

**Supplementary Table:**

**Table S1.** Crystal data and structure refinement for Ag-Bz.

Identification code	Ag-Bz
Empirical formula	$C_{25}H_{42}Ag_5F_3N_2O_2S_4$
Formula weight	1127.19
Temperature/K	235.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.2226(4)

b/Å	24.7501(8)
c/Å	12.0798(4)
$\alpha$ /°	90
$\beta$ /°	102.123(2)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	3572.8(2)
Z	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	2.096
$\mu$ /mm <sup>-1</sup>	24.138
F(000)	2192.0

**Table S2.** MALDI-TOF-MS data of Ag-Bz solution.

Assignment	Exp.	Sim.
$[\text{Ag}_5(\text{CF}_3\text{COO})(\text{S}^t\text{Bu})_4(\text{Bz})(\text{MeOH})_3+\text{H}]^+$	1224.606	1224.333
$[\text{Ag}_5(\text{CF}_3\text{COO})_2(\text{S}^t\text{Bu})_4(\text{Bz})(\text{MeCN})+\text{H}]^+$	1281.669	1281.267
$[\text{Ag}_6(\text{CF}_3\text{COO})(\text{S}^t\text{Bu})_4(\text{Bz})_2(\text{MeOH})_3+\text{H}]^+$	1443.841	1443.459

**Table S3.** FL data of Ag-Bz in different solution.

	Em (nm)	Quantum yield (%)	Lifetimes (ns)
EtOH	603	2.000	47.67891
MeOH	603	2.631	69.05984
Ethylene glycol	603	3.077	81.57576

### References

1. B. Li, R.-W. Huang, J.-H. Qin, S.-Q. Zang, G.-G. Gao, H.-W. Hou and T. C. W. Mak, *Chemistry – A European Journal*, 2014, **20**, 12416-12420.