Supporting Information

Rational assembly and luminescence properties of 2 and 3D organometallic networks using silver(I) 4-pyridylethynide and 5-pyrimidylethynide complexes as building units

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S1. Synthesis and characterization of 4

S2. Crystal data for 4

S3. Figure S1 and S2 (Crystal structure of 4)

S4. Emission spectrum for 4-ethynlypyridine in solid state (Figure S3)
S1. Synthesis and characterization of 4

To a 4 mL vial containing solid 5-ethynylpyrimidine (0.0024g, 0.023 mmol), two drops of distilled water and solid silver nitrate in excess (0.0094 g, 0.056 mmol) were added. This mixture was stirred for 20 minutes to generate a white precipitate. After washing with distilled water two times to remove nitric acid released from the reaction and excess AgNO₃, and exchanging anion with ammonium tetrafluoroborate (0.10 g, 0.954 mmol), an off-white solid was obtained. This solid was dissolved in a concentrated solution of silver trifluoroacetate (0.4 mL distilled water, 0.0119 g CF₃CO₂Ag, 0.058 mmol) by heating to give a clear solution. This solution was placed in a desiccator charged with P₂O₅, and colorless crystals were obtained in about 20% yield in several days (0.0041g). Elemental analysis (%) calcd for C₁₂H₉N₂O₉F₉Ag₄ (927.69): C 15.54, H 0.98, N 3.02; found: C 15.26, H 0.91, N 2.88. IR: 1684 cm⁻¹ (vs, ν(CF₃CO₂⁻)).

S2. Crystal data for 4

(5-Pyrim-C₂Ag)-3CF₃CO₂Ag·3H₂O, C₁₂H₉N₂O₉F₉Ag₄, M = 927.69, orthorhombic, space group Pbca, a = 15.5338(4) Å, b = 16.0601(5) Å, c = 17.2227(6) Å, α = 90°, β = 90°, γ = 90°, V = 4296.6(2) Å³, Z = 8, T = 298 K, Dc = 2.868 g cm⁻³, μ = 3.720 mm⁻¹, F(000) = 3488. A total of 39346 reflections (4910 independent, Rint = 0.1082) were measured. Final agreement indices were R₁ = 0.0394, wR₂ = 0.0855 and a goodness-of-fit = 0.945 for 417 parameters and 4910 reflections [I >2σ(I)]. Two CF₃ (C₈, C₁₀) in trifluoroacetate groups are disordered and processed into two parts.

S3. Figure S1 and S2 (Crystal structure of 4)

Fig. S1 a) Coordination mode I of 5-pyrimidylethynide ligand in 3 (50% thermal ellipsoids); b) 2D coordination network of 3, viewed along the b direction; c) 2D layers viewed along the a direction. All the hydrogen atoms and CF₃CO₂⁻ groups are omitted for clarity. Symmetry code: A -0.5+x, 0.5-y, -z; B x, 0.5-y, 0.5+z. Selected bond lengths [Å] and angles [deg]: C₅-C₆ 1.208(6), C₅-Ag₄A 2.534(4), C₆-Ag₁A 2.358(5), C₆-Ag₂A 2.203(5), C₆-Ag₃A 2.238(5), C₆-Ag₄A 2.496(5), N₁-Ag₁ 2.389(4), N₂-Ag₃B 2.316(4), O₁WA-Ag₁A 2.484(4), O₁WA-Ag₁ 2.683,
S3. Emission spectrum for 4-ethylpyridine in solid state

Fig. S3 Solid state emission spectrum of 4-ethylpyridine in solid state (λ<sub>ex</sub> 372 nm) at room temperature.