

Ag^I/V^V heterobimetallic frameworks generated from novel-type {Ag₂(VO₂F₂)₂(triazole)₄} secondary building blocks: a new aspect in the design of SVOF hybrids.

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A series of new silver(I)-containing MOFs [Ag₂(tr₂ad)₂](ClO₄)₂ (**1**), [Ag₂(VO₂F₂)₂(tr₂ad)₂]·H₂O (**2**), [Ag₂(VO₂F₂)₂(tr₂eth)₂(H₂O)₂] (**3**), and [Ag₂(VO₂F₂)₂(tr₂cy)₂]·4H₂O (**4**) supported by 4-substituted bifunctional 1,2,4-triazole ligands (tr₂ad = 1,3-bis(1,2,4-triazol-4-yl)adamantane, tr₂eth = 1,2-bis(1,2,4-triazol-4-yl)ethane, tr₂cy = trans-1,4-bis(1,2,4-triazol-4-yl)cyclohexane) were hydrothermally synthesized and structurally characterized. In these complexes, the triazole heterocycle as an N¹,N²-bridge links either two adjacent Ag–Ag or Ag–V centers at short distances forming polynuclear clusters. The crystal structure of compound **1** is based on cationic {Ag₂(tr)₄}²⁺ fragments connected in a 2D rhombohedral grid network with (4,4) topology. The neighboring layers are tightly packed into a 3D array by means of argentophilic interactions (Ag...Ag 3.28 Å). Bridging between different metal atoms through the triazole groups assists formation of heterobimetallic Ag^I/V^V secondary building blocks in a linear V–Ag–Ag–V sequence that is observed in complexes **2–4**. These unprecedented tetranuclear {Ag₂(VO₂F₂)₂(tr)₄} units (the intermetal Ag–Ag and Ag–V distances are 4.24–4.36 and 3.74–3.81 Å, respectively), in which vanadium(V) oxofluoride units possess distorted trigonal bipyramidal environment {VO₂F₂N}[–], are incorporated into 1D ribbon (**2**) or 2D square nets (**3**, **4**) using bitopic μ₄-triazole ligands. The valence bond calculation for vanadium atoms shows +V oxidation state in the corresponding compounds. Thermal stability and photoluminescence properties were studied for all reported coordination polymers.

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