Supplementary Information

Four di-Cu\textsuperscript{II}-substituted sandwich-type germanomolybdates obtained under different reaction conditions: from zero-dimensional to two-dimensional structure

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Scheme. S1 The unusual $[\beta$-Y-GeMo\textsubscript{9}O\textsubscript{33}]\textsuperscript{8–} unit derives from the well-known $[\beta$-GeMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{4–}.

Fig. S1 The space packing diagram of 4.

Fig. S2 The IR spectra of 1–4.

Fig. S3 The UV spectra of 1–4.

Fig. S4 The TG curve of 4.

Fig. S5 (a) Temperature dependence of the $\chi_M$ and $\chi_M T$ for polycrystalline samples of 1 at a 2 kOe applied field; (b) The temperature evolution of the inverse magnetic susceptibility $\chi_M^{-1}$ for 1 between 50 and 300K. The red solid lines are generated from the best fit by the Curie-Weiss expression with the Curie constant $C = 0.77$ cm\textsuperscript{3} mol\textsuperscript{-1} K and the Weiss constant $\theta = -17.46$ K.

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The magnetic susceptibility of 1 was obtained on polycrystalline samples in the temperature range 2–300 K. The temperature dependence of $\chi_M$ and $\chi_M T$ product of 1 under a constant magnetic field of 20 KOe is shown in Figure S5a. Upon cooling, the $\chi_M$ value gradually increases to a maximum of $1.14 \times 10^{-2}$ cm$^3$ mol$^{-1}$ at 34.7 K, and then rapidly decreases to a minimum of $6.72 \times 10^{-3}$ cm$^3$ mol$^{-1}$ at 9.7 K, when the temperature is further lowered, a sudden increase of the $\chi_M$ value occurs which can be ascribed to some paramagnetic impurities.\textsuperscript{1} The $\chi_M T$ of 0.72 cm$^3$...
mol\(^{-1}\) K at 300K is consistent with the expected spin-only value of 0.75 cm\(^3\) mol\(^{-1}\) K for two isolated Cu\(^{II}\) ions (S = \(1/2\)) with \(g = 2.00\). With the temperature decreasing, the \(\chi_M T\) value decreases slowly up to 104 K and then sharply to 0.05 cm\(^3\) mol\(^{-1}\) K at 7 K. This magnetic behavior typifies the antiferromagnetic coupling interactions between adjacent Cu\(^{II}\) centers, which is confirmed by the negative Curie-Weiss constant \(\theta = -17.46\) K (Fig. S5b). The classical correlation between the experimental exchange constant and the Cu–O–Cu bond angle (\(\alpha\)) reveals that the compounds are generally antiferromagnetic for \(\alpha > 98^\circ\), whereas ferromagnetic for \(\alpha < 98^\circ\).\(^1\) The fact that the Cu–O–Cu angle of 99.3(3)\(^\circ\) in 1 is larger than 98\(^\circ\) indicates that the weak antiferromagnetic interaction is expected and is in accordance with the simulated result.
