

Electronic Supplementary Information (ESI)

The first metal-organic framework containing an unprecedented *in situ*-generated C-substituted hexamethylenetetramine ligand

Zhao-Peng Deng,^a Li-Hua Huo,^a Hui Xu,^a Hui Zhao,^a Seik Weng Ng^b and Shan Gao^{*a}

- Fig. S1.** 1-D chain formed via connecting Ag1 atoms by the fba ligands with alternate Ag₂O₂ rings and Ag₂C₂O₄ rings.
- Fig. S2.** 1-D chain formed via connecting Ag2 atoms by the cphmt ligands with protrudent Ag1 atoms.
- Fig. S3.** 2-D tubelike network, built from the combination of two kinds of chains *via* N1 atom of cphmt ligand. The carbon atoms of hmt section in the new generated ligands denoted as gray ball.
- Fig. S4.** 3-D framework of **1** formed by aqua ligand supporting the 2-D networks viewed along the *a*-axis. The bridging oxygen atoms of aqua ligand denoted as green ball.
- Fig. S5.** TG curves for complex **1** under N₂ atmospheric pressure.
- Scheme S1** Proposed mechanism for the formation of *in-situ* generated ligand.
- Table S1** Crystal data and structure refinement parameters of complex **1**
- Table S2** Selected bond distances (Å) data of complex **1**

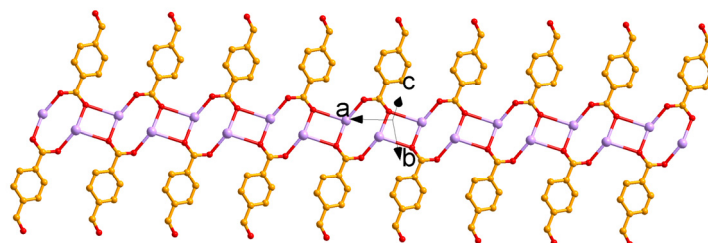


Fig. S1 1-D chain formed via connecting Ag1 atoms by the fba ligands with alternate Ag₂O₂ rings and Ag₂C₂O₄ rings.

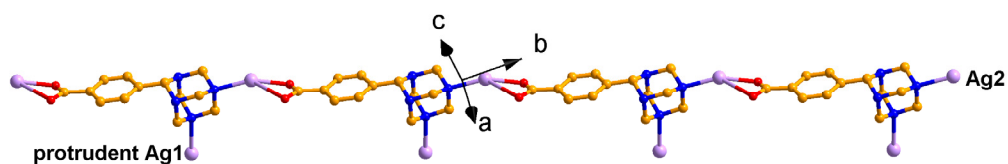


Fig. S2 1-D chain formed via connecting Ag2 atoms by the cphmt ligands with protrudent Ag1 atoms.

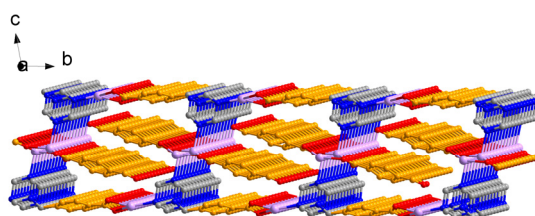


Fig. S3 2-D tubelike network, built from the combination of two kinds of chains via N1 atom of cphmt ligand. The carbon atoms of hmt section in the new generated ligands denoted as gray ball.

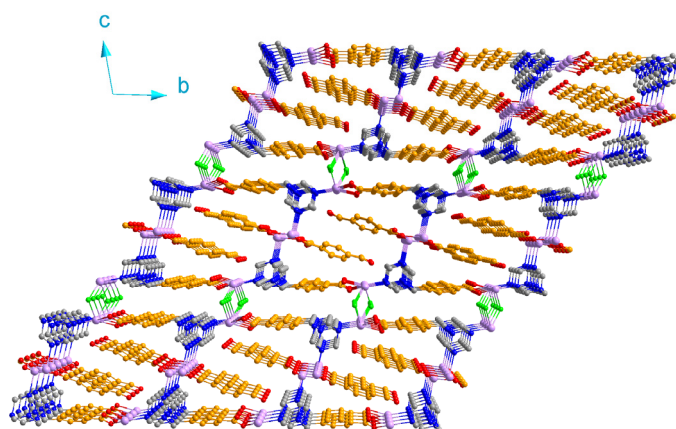


Fig. S4 3-D framework of **1** formed by aqua ligand supporting the 2-D networks viewed along the *a*-axis. The bridging oxygen atoms of aqua ligand denoted as green ball.

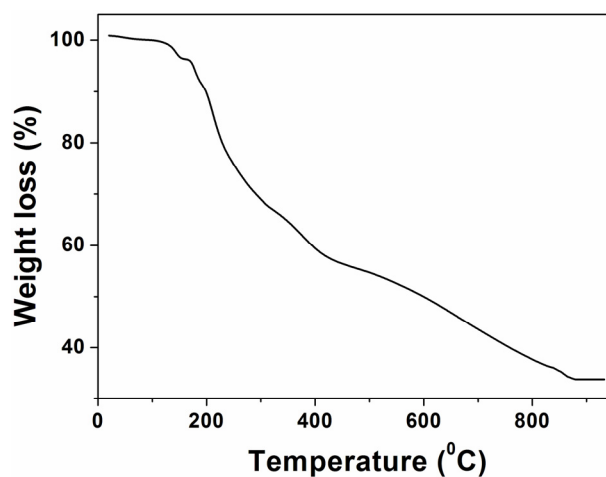
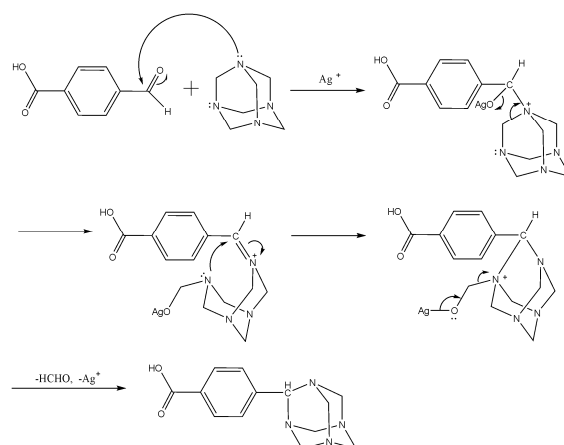


Fig. S5 TG curves for complex **1** under N₂ atmospheric pressure.



Scheme S1 Proposed mechanism for the formation of *in-situ* generated ligand.

Proposed mechanism for the formation of *in situ*-generated cphmt ligand was suggested as shown in Scheme S1. The ultimate result can be simply viewed as a substitution, *i.e.* a -CH₂- group in hmt was replaced by a HOOC-Ph-CH- group. By contrast, such C-substituted hmt ligand was not found in the similar system with Cd(II), Cu(II), Zn(II) metal salts. Thus, the silver(I) ion may play a crucial role in the entire process. Furthermore, silver mirror phenomenon was observed in the reaction system which may suggest the existence of the byproduct HCHO.

Table S1 Crystal data and structure refinement parameters of complex **1**

Empirical formula	C ₂₁ H ₂₂ N ₄ O ₆ Ag ₂
Formula weight	642.17
Crystal system	Triclinic
Space group	P $\bar{1}$
<i>a</i> /Å	6.0834(5)
<i>b</i> /Å	12.8715(11)
<i>c</i> /Å	13.5851(12)
α ^o	101.212(3)
β ^o	91.969(3)
γ ^o	97.795(2)
<i>V</i> /Å ³	1031.78(15)
<i>Z</i>	2
<i>D_c</i> /mg m ⁻³	2.067
μ /mm ⁻¹	1.948
θ range	3.06 to 25.00
Reflections collected/unique [R(int)]	7882/3585 [0.0455]
<i>F</i> (000)	636
R1, wR2 [I > 2 σ (I)]	0.0697, 0.1870
R1, wR2 [all data]	0.0978, 0.2196
GOF	1.094

Table S2 Selected bond distances (Å) data of complex **1**^a

Ag(1)-O(3)	2.199(7)	Ag(2)-O(1)	2.205(8)
Ag(1)-O(4) ⁱ	2.272(7)	Ag(2)-O(2)	2.949(11)
Ag(1)-N(1)	2.414(7)	Ag(2)-N(2) ⁱⁱ	2.211(8)
Ag(1)-O(4) ^v	2.798(7)	Ag(2)-O(1W)	2.434(11)
Ag(1)-Ag(1) ⁱ	2.9343(18)	Ag(2)-O(1W) ⁱⁱⁱ	2.786(11)

^a Symmetry operation: i, -x+3, -y+1, -z+1; ii, x-1, y-1, z; iii, -x+1, -y, -z+2 ; v, x-1, y, z.