## Supporting Information

# An unusual three-dimensional self-penetrating network derived from cross-linking of twofold interpenetrating nets via ligand-unsupported Ag–Ag bonds: synthesis, structure, luminescence, and theoretical study †

**Xue-Zhi Song,[ab] Chao Qin,[a] Wei Guan,[a] Shu-Yan Song*[a] and Hong-Jie Zhang*[a]**

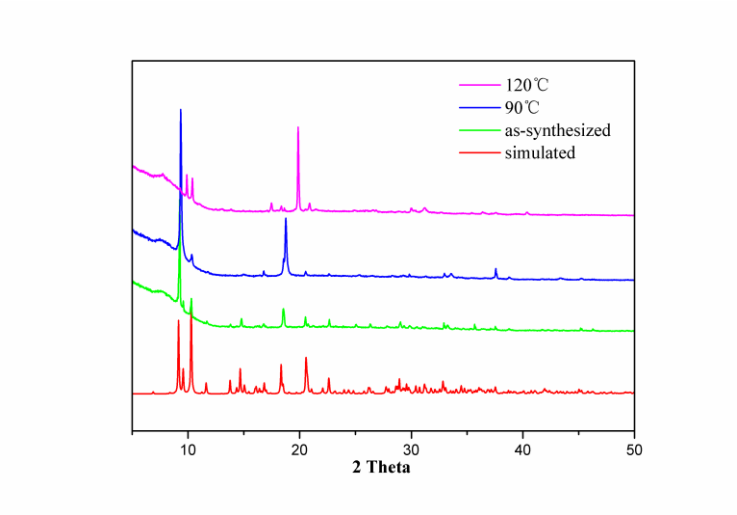


**Fig. S1.** PXRD patterns of **1**: simulated, as-synthesized, treated at 90 °C and 120 °C, respectively.

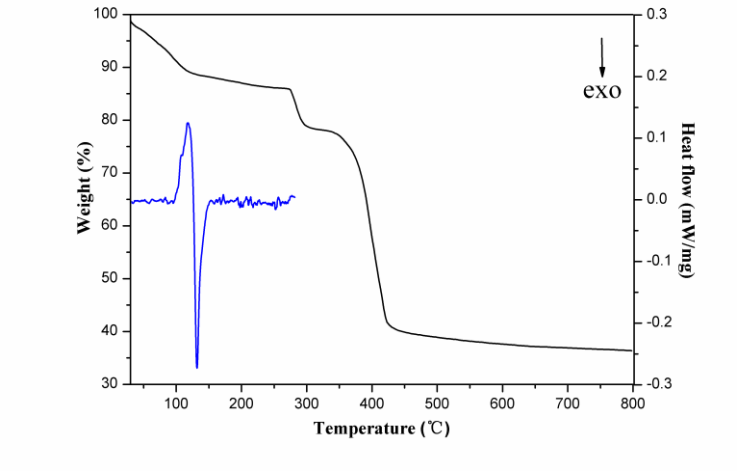


**Fig. S2.** TG and DSC curves of compound **1**.

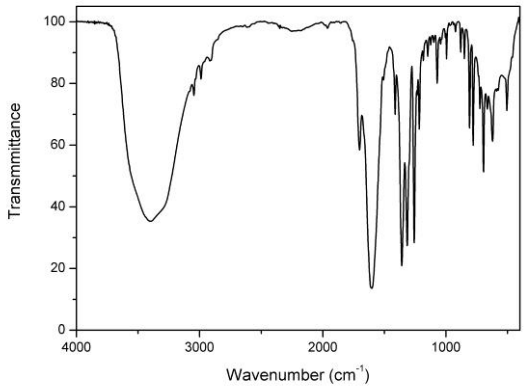


**Fig. S3.** IR spectrum of compound **1**.

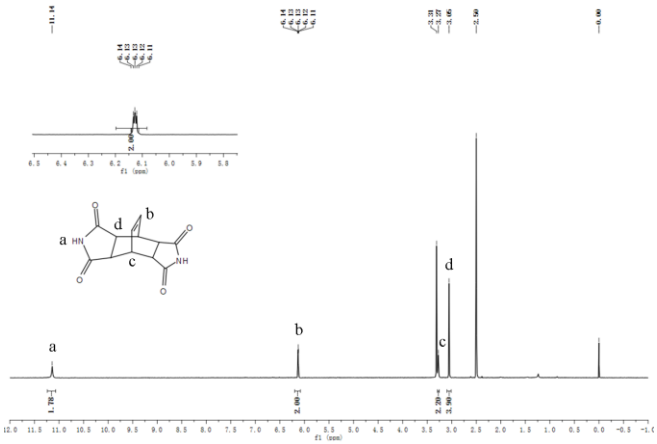


**Fig. S4.** $^{1}H$ NMR spectrum of $H_2L$ ligand.

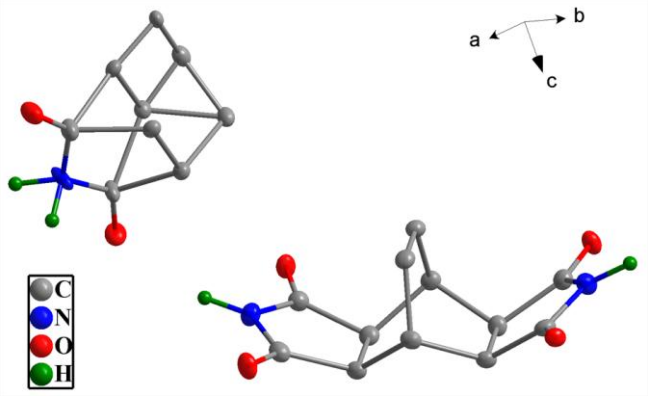


**Fig. S5.** View of the asymmetric unit of $H_2L$ ligand.

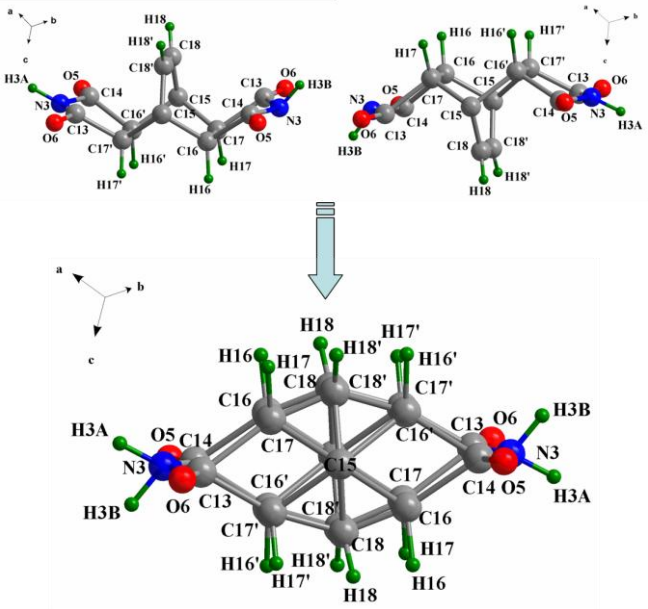


**Fig. S6.** Schematic view of the disordered part of $H_2L$ ligand.

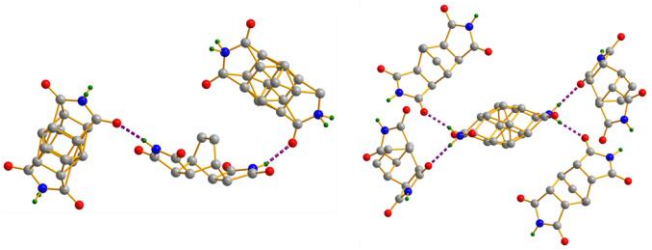

**Fig. S7.** Hydrogen bonds in $H_2L$ ligand.

**Table S1:** Crystallographic data for $H_2L$.

| | **$H_2L$** |
|---|---|
| Empirical formula | $C_{12}H_{10}N_2O_4$ |
| *M* | 246.22 |
| T/K | 123(2) |
| λ/ Å | 0.71073 |
| crystal system | monoclinic |
| space group | $P2_1/n$ |
| *a*/ Å | 7.6395(4) |
| *b*/ Å | 21.1972(11) |
| *c*/ Å | 9.8455(5) |
| *α*/ deg | 90 |
| *β*/ deg | 97.6830(10) |
| *γ*/ deg | 90 |
| *V*/ Å$^3$ | 1580.03(14) |
| *Z* | 6 |
| $\mu$/mm$^{-1}$ | 0.119 |
| $R1^a$ [$I > 2\sigma(I)$] | 0.0630 |
| $wR2^b$ [$I > 2\sigma(I)$] | 0.1343 |
| GOF on $F^2$ | 1.118 |

$^aR_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $^bwR_2 = \Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$

**Table S2:** Hydrogen bonds for $H_2L$.

| D-H…A | *d*(D-H)/Å | *d*(H...A)/Å | *d*(D...A)/Å | <(DHA)/deg |
|---|---|---|---|---|
| N(2)-H(2N)...O(5) | 0.92(4) | 2.06(4) | 2.944(4) | 161(4) |
| N(3)-H(3A)...O(1)#1 | 0.899(11) | 2.104(17) | 2.995(4) | 171(7) |
| N(3)-H(3B)...O(2)#2 | 0.901(10) | 2.003(18) | 2.896(4) | 170(7) |
| N(1)-H(1N)...O(6)#3 | 0.96(4) | 1.93(4) | 2.879(4) | 170(4) |

Symmetry transformations used to generate equivalent atoms: #1 = -x+3/2,y-1/2,-z+3/2; #2 = -x+1,-y+2,-z+2; #3 = -x+1/2,y+1/2,-z+3/2.

**Text S1:** Description and discussion of $H_2L$ crystal structure.

There are two independent molecules of $H_2L$, one of which lies disordered about an inversion center. We drew a picture in order to show this disorder clearly (Fig. S6). In the crystal, the regular $H_2L$ molecule interacted with two adjacent disordered $H_2L$ molecules through N-H…O hydrogen bonds. While one disordered $H_2L$ molecule and four adjacent regular $H_2L$ molecules are maintained together through four disordered H atoms arising from the disordered $H_2L$ ligand with the oxygen atoms from regular $H_2L$. The hydrogen bonds are shown in Fig. S7 and listed in Table S2.