Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information for

Luminescent $Ag_8(DPPY)_6(PhC{\equiv}C)_6Cl_6$ with a Triangular Superatomic Ag_8 Core

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Table S1. Crystal data for the $[Ag_8(DPPY)_6(PhC{\equiv}C)_6]$ cluster.

Identification code	mx8857a
Empirical formula	$C_{152}H_{116}Ag_8Cl_6N_6P_6$
Formula weight	3287.92
Temperature	110.01(10)K
Crystal system	trigonal
Space group	R32
Unit cell dimensions	a = 17.4780(3)Å α = 90° b = 17.4780(3) Å β = 90° c = 39.6944(7) Å γ = 120°
Volume	10501.3(4)Å^3
Z	3.00006
Density (calculated)	1.560 Mg/m^3
Absorption coefficient	1.330 mm^{-1}
F(000)	4914.0
Crystal size	0.28 × 0.25 × 0.23mm^3
Theta range for data collection	2.88 to 54.994°
Index ranges	-39 ≤ h ≤ 39, -39 ≤ k ≤ 39, -48 ≤ l ≤ 50
Reflections collected	33066
Independent reflections	5395 [R(int) = 0.0182]
Completeness to theta = 27.424°	99.09%
Absorption correction	Semi-empirical From equivalents
Max. and min. transmission	1.0000 and 0.90394
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	5395/0/269
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R_1 = 0.0196, wR_2 = 0.0584
R indices (all data)	R_1 = 0.0198, wR_2 = 0.0587
Extinction coefficient	n/a
Largest diff. peak/hole	0.40/-1.54 e.Å^{-3}

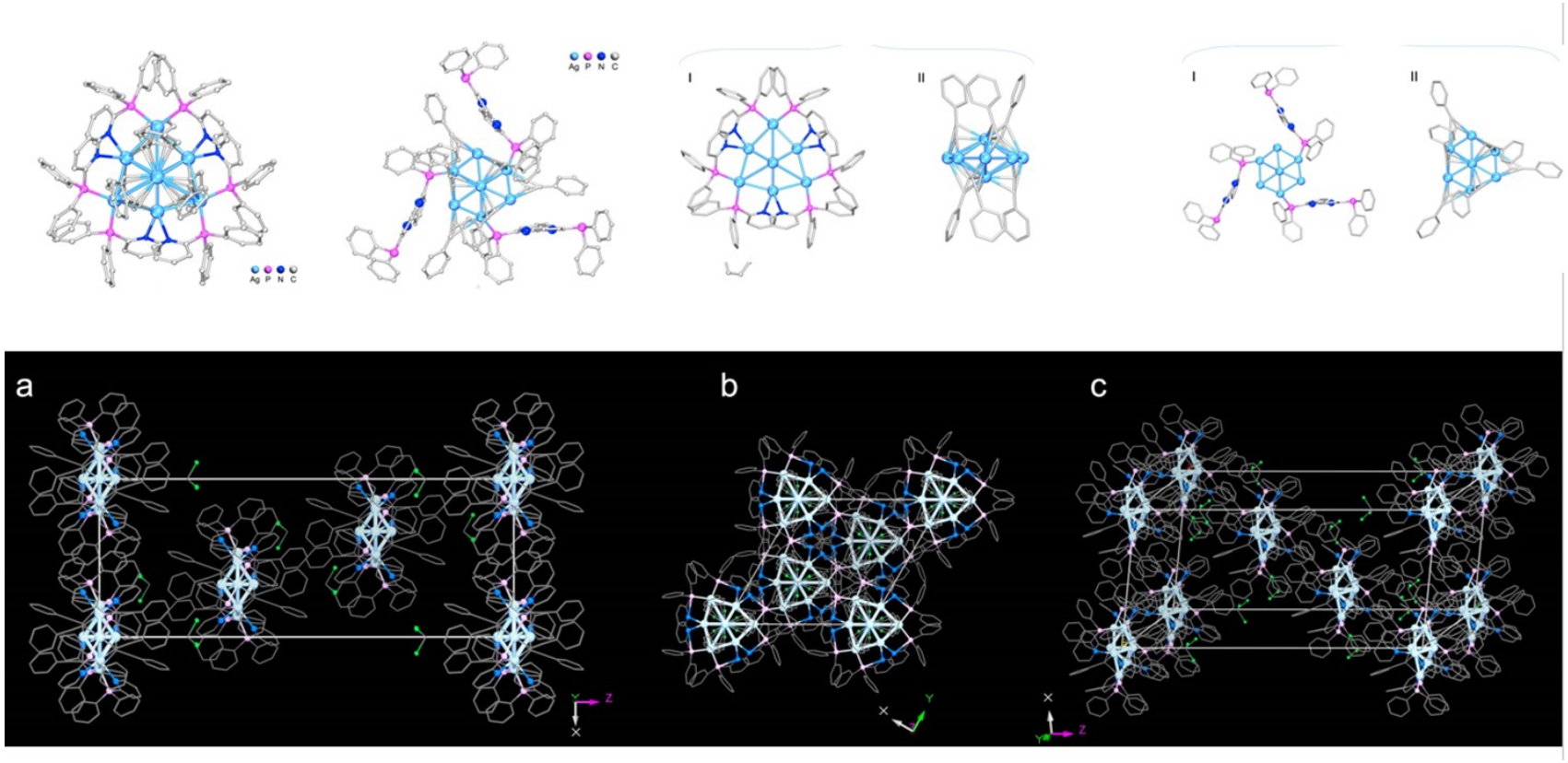

Fig. S1 The single-crystal structure, coordination behavior, and the packing modes of the $Ag_8(DPPY)_6(PhC{\equiv}C)_6$ cluster.

In addition to the improved structural stability observed due to the nature of ligand coordination to Ag atoms in the cluster, a thermal stability test was performed with thermogravimetric analysis (TGA) to determine the thermal strength of the cluster through thermal decomposition and weight loss in N_2 atmosphere shown in (Fig. S2). The cluster, first of all, undergoes step-wise decomposition showing a two-step thermal decomposition with a minor weight loss of 1.72% in the first step and a significant weight loss of 70.56% in the second step. The total weight loss is 72.28%. The major decomposition in the second phase begins at about 200^0C, indicating thermal stability around 200^0C.

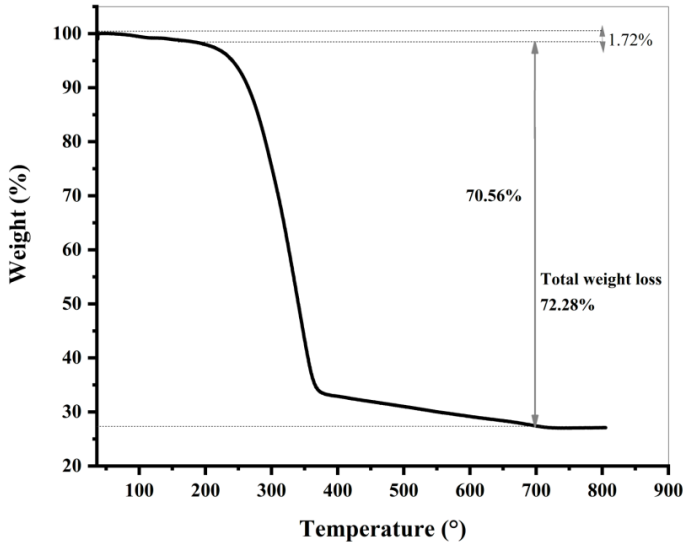

Fig. S2 Thermogravimetric analysis of $Ag_8(DPPY)_6(PhC{\equiv}C)_6$ cluster in N_2 atmosphere.

To determine the oxidation state of Ag atoms, we conducted an XPS experiment in this regard using the binding energies and chemical shifts in XPS spectra (Fig. S3). We determined the Ag and P oxidation state in the surface region. The XPS spectrum of Ag 3d shows two peaks at binding energy values of 367.66 and 373.67 eV corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ (Fig. S3b), suggesting the Ag valence state as Ag (I). Moreover, the binding energy of P, 2p3/2 shows the peak at 131.07 eV is a characteristic of metal phosphate indicative of chemisorbed P species (Fig. S3c); the C 1s peak was located at 285.7 eV, corresponding to the natural character of the ligand chain (Fig. S3a).

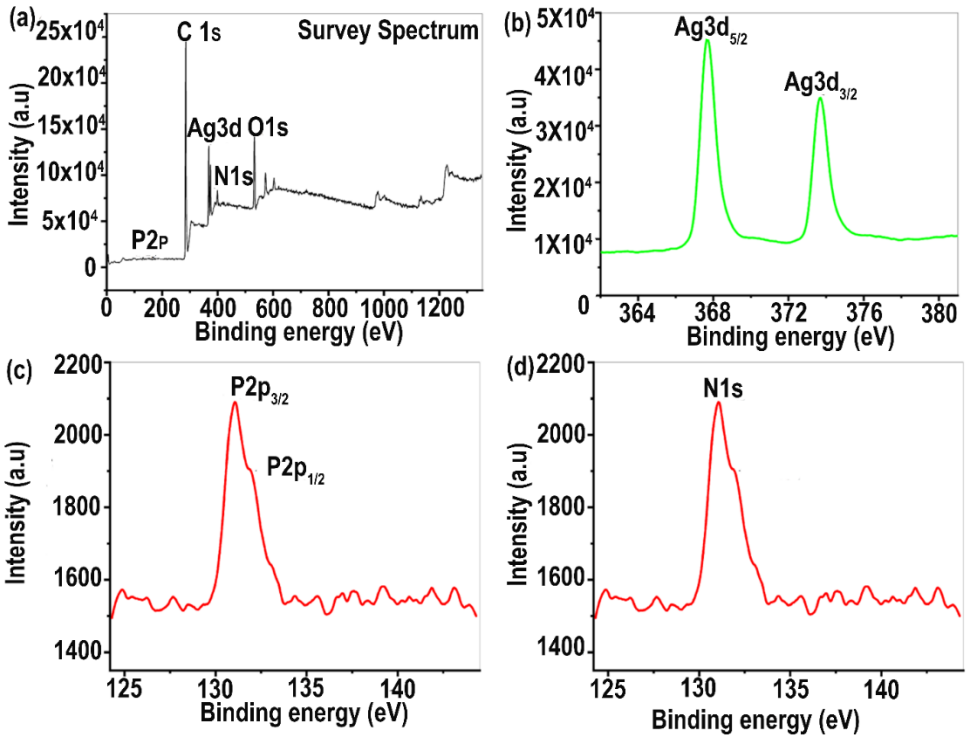

Fig. S3 The XPS survey spectrum (a), and the XPS patterns of Ag 3d (b) and P 2p(c) and N 1s (d) of the $[Ag_8(DPPY)_6(PhC{\equiv}C)_6]$ cluster.