## **Electronic Supplementary Information (ESI)**

# A Hexadecanuclear Silver Alkynyl Cluster Based NbO Framework with Triple Emissions from Visible to Near-Infrared II Region

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### **Materials and Instruments**

All reagents employed were commercially available and used as received without further purification. The solvents were purified and distilled by standard procedures prior to use. IR spectra were recorded on a Bruker ALPHA in the frequency range of 4000-400 cm<sup>-1</sup>. The elemental analyses (C and H) were determined on a Vario EL III analyzer. Morphology of the samples and elemental composition analyses were measured using an SU-8010 field emission scanning electron microscope (FESEM; Hitachi Ltd., Tokyo, Japan) equipped with an Oxford-Horiba Inca XMax50 energy dispersive X-ray spectroscopy (EDS) attachment (Oxford Instruments Analytical, High Wycombe, England). Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with CuKa radiation equipped with an X'Celerator detector. The diffuse-reflectance spectra were recorded on a UV/Vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific) using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere. The excitation spectra were recorded on a Lumina Fluorescence Spectrometer (Thermo Fisher) at the emission wavelength of 630 nm. Temperature-dependent photoluminescence measurements were carried out in an Edinburgh spectrofluorimeter (F920S) coupled with an Optistat DN cryostat (Oxford Instruments), and the ITC temperature controller and a pressure gauge were used to realize the variable-temperature measurement in the range of 90-290 K. Spectra were collected at different temperatures after a 5min homoiothermy. Time-resolved photoluminescence lifetime measurements were measured on Edinburgh spectrofluorimeter (F920S) using a timecorrelated single-photon counting technique. Mass spectra were recorded on an Agilent 6224 (Agilent Technologies, USA) ESI-TOF-MS spectrometer. Sample solutions are infused by a syringe pump at 4  $\mu$ L/min. Data were acquired using the following settings: ESI capillary voltage was set at 4000 V (+) ion mode and 3500 V (-) ion mode and fragmentor at 200 V. The liquid nebulizer was set to 15 psig and the nitrogen drying gas was set to a flow rate of 4 L/min. Drying gas temperature was maintained at 150 °C. The data analyses of mass spectra were performed based on the isotope distribution patterns using Agilent MassHunter Workstation Data acquisition software (Version B.05.00). The reported m/z values represent monoisotopic mass of the most abundant peak within the isotope pattern.

### X-ray Crystallography

Single crystal of **SD**/**Ag18** of appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Intensity data and cell parameters were recorded at 298 K on a Bruker Apex II single crystal diffractometer, employing a Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.<sup>1</sup> The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*<sup>2</sup> and refined by full-matrix least-squares techniques against  $F_0^2$  using the SHELXL program<sup>3</sup> through the OLEX2 interface.<sup>4</sup> Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. All structures were examined using the Addsym subroutine of PLATON<sup>5</sup> to ensure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table S1. Selected bond lengths and angles are collated in

### Synthesis

**Caution!** Due to the explosive nature of silver alkynyls, great care should be taken and only small amounts should be used.

### Synthesis of [cPrC≡CAg]<sub>n</sub>.

Ethynylcyclopropane (24.0 mmol, 2.0 mL) in ethanol (15 mL) was added to  $Ag_2O$  (13.0 mmol, 3.0 g) in ammonia solution (60 mL). The mixture was stirred for 1 h, then the white solid (3.9 g, 93.3%) was collected by vacuum filtration, then washed with EtOH and Et<sub>2</sub>O.

### Synthesis of SD/Ag18.

cPrC=CAg (0.1 mmol, 17.3 mg) was added to a MeOH/MeCN (v:v = 3:2) solution containing AgBF<sub>4</sub> (0.08 mmol, 15 mg), the resulting solution was treated by ultrasound in a KQ5200DE ultrasonic instrument (70 W, Kun Shan Ultrasonic Instruments Co.) for 20 minutes at room temperature to give a turbid solution. Then 20 µL TMEDA was added in above mixture that was treated by ultrasound for another 20 minutes. The pale yellow filtrate was left to stand in the dark at room temperature. After three days, pale yellow crystals were deposited with a yield of 55 %. **SD/Ag18** can be also synthesized by solvothermal method (see below) but with a very low yield of 15 %. cPrC=CAg (0.1 mmol, 17.3 mg) and AgBF<sub>4</sub> (0.08 mmol, 15 mg) was dissolved in 5 mL MeOH/MeCN (v:v = 3:2) solution. The resultant solution was further stirred for 30 minutes along with adding 20 µL TMEDA. The final mixture was transferred to a 25 mL Teflon-lined stainless steel autoclave and keep at 70 °C for 2000 minutes. The pale yellow filtrate was left to stand in the dark at room temperature. After 5 days, tiny pale yellow crystals were deposited at the bottom of the bottle. Anal. Calcd for C<sub>80</sub>H<sub>80</sub>Ag<sub>18</sub>CIBF<sub>4</sub> calcd (found): C, 30.94 (31.80); H, 2.60 (2.57) %. IR: 3002 (w), 2015 (m), 1329 (m), 1047 (s), 938 (s), 808 (m), 762 (w) 507 (w) cm<sup>-1</sup>.

Compound	SD/Ag18
Empirical formula	C <sub>80</sub> H <sub>80</sub> Ag <sub>18</sub> Cl
Formula weight	3018.54
Temperature/K	298
Crystal system	cubic
Space group	Pn-3n
a/Å	23.686(5)
b/Å	23.686
c/Å	23.686
α/°	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å <sup>3</sup>	13289(8)
Ζ	6
$\rho_{calc}g/cm^3$	2.263
μ/mm <sup>-1</sup>	3.943
F(000)	8538.0
Radiation	MoKα ( $\lambda$ = 0.71073)
2\Theta range for data collection/°	3.438 to 49.984
Index ranges	$-21 \le h \le 22, -17 \le k \le 28, -28 \le l \le 28$
Reflections collected	35925
Independent reflections	1965 [R <sub>int</sub> = 0.2211, R <sub>sigma</sub> = 0.0807]
Data/parameters	1965/0/113
Goodness-of-fit on F <sup>2</sup>	1.012
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0637, wR_2 = 0.1519$
Final R indexes [all data]	$R_1 = 0.1605, wR_2 = 0.2347$
Largest diff. peak/hole/eÅ-3	1.32/-0.87

 Table S1: Crystal Data Collection and Structure Refinement for SD/Ag18.

Ag1—Ag1 <sup>i</sup>	3.221 (3)	Ag1—C6	2.07 (2)		
Ag1—Ag2 <sup>ii</sup>	2.930 (2)	Ag2—C1 <sup>i</sup>	2.48 (2)		
Ag1—Ag2	2.956 (2)	Ag2—C6 <sup>iii</sup>	2.25 (2)		
Ag1—Ag2 <sup>i</sup>	3.144 (3)	Ag2—C6	2.302 (19)		
Ag1—Ag3	3.0148 (15)	Ag3—C1 <sup>iv</sup>	2.48 (2)		
Ag1—C1	2.04 (3)	Ag3—C1	2.48 (2)		
C1—Ag1—C6	171.9 (8)	C6 <sup>iii</sup> —Ag2—C6	135.6 (11)		
C6 <sup>iii</sup> —Ag2—C1 <sup>i</sup>	111.1 (7)	C1—Ag3—C1 <sup>v</sup>	110.3 (6)		
C6—Ag2—C1 <sup>i</sup>	107.5 (7)	C1—Ag3—C1 <sup>iv</sup>	107.9 (12)		
Symmetry codes: (i) $-x+3/2$ , z, y; (ii) x, $-z+1/2$ , y; (iii) x, z, $-y+1/2$ ; (iv) $-x+3/2$ , $-y+1/2$ , z; (v)					
y+1/2, -x+1, -z+1.					

Table S2: Selected bond lengths (Å) and angles (°) for SD/Ag18.

Figure S1: The IR spectra of SD/Ag18 and NaBF<sub>4</sub>.





Figure S2: The coordination environments of Ag1-Ag3 in SD/Ag18.

- **Ag1**: Two-coordinated linearity;
- Ag2: three-coordinated triangle;
- Ag3: four-coordinated tetrahedron.

Figure S3: The four-layer motif of Ag<sub>16</sub> unit in SD/Ag18.



Figure S4: The drum-like polyhedral skeleton of Ag<sub>16</sub> unit in SD/Ag18.



Two tetragons at drumheads up and down and 24 trigons at the cylindrical body.



### Figure S5: The positive ion mode ESI-MS of SD/Ag18 dissolved in DCM. (Black

line: experimental data, red lines: profile lines of the simulated isotope patterns.)

Species	Assignment	Exp.	Sim.
1a	$[Ag_{16}(cPrC=C)_{13}Cl]^{2+}$	1303.46	1303.48
1b	$[Ag_{17}(cPrC=C)_{14}Cl]^{2+}$	1390.43	1390.45
1c	$[Ag_{18}(cPrC=C)_{15}Cl]^{2+}$	1476.40	1476.42
1d	$[Ag_{19}(cPrC=C)_{16}Cl]^{2+}$	1563.37	1563.39
1e	$[Ag_{20}(cPrC=C)_{17}Cl]^{2+}$	1649.34	1649.37
1f	$[Ag_{22}(cPrC=C)_{17}Cl_3(H_2O)_3]^{2+}$	1820.26	1820.26
1g	$[Ag_{14}(cPrC=C)_{12}Cl]^+$	2326.08	2326.11
1h	$[Ag_{15}(cPrC=C)_{13}Cl]^+$	2500.01	2500.05
1i	$[Ag_{16}(cPrC=C)_{14}Cl]^+$	2671.95	2672.00
1j	$[Ag_{17}(cPrC=C)_{15}Cl]^+$	2845.90	2845.94
1k	$[Ag_{18}(cPrC=C)_{16}Cl]^+$	3017.87	3017.88

Table S3: The assigned formulae of the key species of SD/Ag18.

Figure S6: The positive ion mode ESI-MS of mother liquid after the ultrasonic



synthesis of SD/Ag18.

Figure S7: The UV-Vis spectrum of SD/Ag18 in the solid state (Inset: Adsorption spectrum of SD/Ag18 derived from the diffuse reflectance spectrum through Kubelka-Munk function.).



The UV-Vis absorption spectrum of **SD/Ag18** was measured in the solid state at room temperature using diffuse reflectance mode. As shown in Figure S7, **SD/Ag18** exhibits double-hump absorptions at 350 and 410 nm, respectively. Based on the transformed Kubelka–Munk plot, the HOMO–LUMO gap was determined as 3.14 eV for **SD/Ag18**.

![](_page_14_Figure_0.jpeg)

Figure S8: The excitation spectrum of SD/Ag18 in the solid state ( $\lambda_{em} = 630$  nm).

Figure S9: The Luminescent lifetime of SD/Ag18 in visible region (red line is

![](_page_15_Figure_1.jpeg)

fitting curve).

![](_page_16_Figure_0.jpeg)

fitting curve).

![](_page_16_Figure_2.jpeg)

Figure S11: The correlation between the temperatures and emission intensity of

(a) / = -8137.927 + 1.486x10<sup>6</sup> O  $R^2 = 0.9404$ Intensity (a. u.) Visible region (HE band) О 0 100 110 120 130 140 150 90 Temperature (K) Intensity (a. u.) (d) /= -3323.79*T* + 9.28 x10<sup>5</sup> 0  $R^2 = 0.98666$ Visible region (LE band) 0 100 150 200 250 300 Temperature (K) (c) Intensity (a. u.) /= -8311.27 T + 1.37x10<sup>6</sup> Q  $R^2 = 0.99839$ NIR region 2 90 100 110 120 130 140 150 Temperature (K)

SD/Ag18 (red line is fitting curve).

Figure S12: The compared powder X-ray diffraction patterns.

![](_page_18_Figure_1.jpeg)

Black: The experimental PXRD pattern of **SD/Ag18**. Red: The simulated PXRD pattern of microcrystalline sample of **SD/Ag18**.

![](_page_19_Figure_0.jpeg)

Figure S13: The Morphology of the samples and elemental composition of

SD/Ag18.

Figure S14: The TGA of SD/Ag18.

![](_page_20_Figure_1.jpeg)

### **Computational Details**

### **Electronic structure calculations**

The first-principle density functional theory calculations were carried out in the *ab initio* VASP program.<sup>6</sup> The exchange-correlation (XC) effects were treated by the generalized gradient approximation (GGA) with Perdew Burke Ernzerhof (PBE)<sup>7</sup> formalism. Projector-augmented wave (PAW)<sup>8</sup> method of Blöchl, featuring the accuracy of augmented plane-wave methods as well as the efficiency of the pseudopotential approach, was used to treat electronic wave function. Specially, 4*d* and 5*s* electrons of Ag, 2*s* and 2*p* electrons of C, and 1*s* electrons of H were explicitly treated as valence electrons. Furthermore, the electronic wave function is expanded in plane waves up to a cutoff energy of 500 eV.  $2\times2\times2$  K-point grid was used in the integration in Brillouin zone. DFT+U strategy<sup>9</sup> was used to correct the strongly correlated interaction between Ag atoms. And the U value was identified according to linear response approach (See following information). In the electronic optimization, the convergence of SCF was assumed when the energy difference between two adjacent circle is less than  $1.0\times10^{-5}$  eV. During the ionic relaxation, the convergence criterion of forces was set to 0.02 eV/Å. For the calculations of partial density of states (PDOS), a tetrahedron method with Blöchl corrections<sup>8</sup> were used to identify exact electronic density.

#### **Calculation of U value**

The  $U_{eff}$  of Ag ions was identified by using the linear response approach introduced by Cococcioni et.al.<sup>10</sup> Projector augmented wave (PAW) method,<sup>8</sup> together with Perdew, Burke and Ernzerhof (PBE)<sup>7</sup> functional, was used to describe the exchange-correlation functional between electrons. Meanwhile, valence electrons of Ag, C and H were described by using vanderbilt ultrasoft pseudopotentials with the plane-wave energy cutoff of 50 Ry. And Kinetic energy cutoff (Ry) for charge density and potential is 360 Ry. The 3×3×3 Monkhorst-Pack grid was employed in the sampling of Brillouin zone. Tetrahedron method<sup>9</sup> of Blöchl was used to calculate the occupIn general, the total energy of DFT+U can be described as follow:

$$E_{DFT+U}[n(r)] = E_{DFT}[n(r)] + E_{U}[\{n_{mm}^{l\sigma}\}]$$
Eq(1)

Where  $E_{\text{DFT}}$  represent a total energy from noninteraction Kohn-Sham algorithm;  $E_{\text{U}}$  is Hubbard correction energy.

Furthermore, if neglecting higher-multipolar terms of Coulomb interaction,  $E_{\rm U}$  is written as:

$$E_{U}[\{n_{mm}^{l\sigma}\}] = \frac{U-J}{2} \sum_{l,\sigma} Tr[n^{l\sigma}(1-n^{l\sigma})] = \frac{U_{eff}}{2} \sum_{l,\sigma} Tr[n^{l\sigma}(1-n^{l\sigma})]$$
 Eq(2)

By linear-response approach U method, the linear response function is defined as

In this method, the interacting ( $\chi$ ) and noninteractiong density response functions with respect to localized perturbations were firstly calculated. Thus  $U_{eff}$  can be obtained by following formula (see Eq(4)).

$$U_{eff} = \chi^{-1} - \chi_0^{-1}$$
 Eq(4)

Via changing the rigid potential shifts  $\alpha$ , the bare and self-consistent occupation regression response functions were achieved. Obviously, the interacting ( $\chi$ ) and the noninteracting ( $\chi_0$ ) are the slopes of bare and self-consistent regression response functions (Figure S15), respectively. Therefore, the obtained U<sub>eff</sub> are 8.84 eV for Ag ions of **SD/Ag18**. In this part, the calculations were performed using PWSCF program of ESPRESSO package.<sup>11</sup>

### Figure S15 the curve of *d* occupations vs α.

![](_page_22_Figure_8.jpeg)

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