Supporting Information

An Atomically Precise All-*tert*-Butylethynide-Protected Ag_{51} Superatom Nanocluster with Color Tunability

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Experimental Section

All reagents employed are commercially available and used as received without further purification. ^{t}BuC≡CAg was prepared according to literature procedure.[S1] Elemental analyses for C, H, and N were performed with a PerkinElmer 2400 CHN elemental analyzer. The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker VERTEX 70 spectrometer. The transmission electron microscopy (TEM) image of the nanocluster **Ag_{51}** was obtained with Tecnai G2 F30 (FEI, Holland). The Vis-NIR experiments were carried out on a PE Lambda 750S UV-vis-NIR spectrophotometer. Fluorescent spectra were recorded on a FP-6500 fluorescence spectrometer, using 5 mm path length cuvettes. Luminescence lifetimes measurements were recorded with an Edinburgh FLS 980 Lifetime and Steady State Spectrometer. Crystal data of **Ag_{51}** was collected at 100 K using the radiation wavelength at 0.65250 Å with a MarCCD detector at beamline BL17B of the Shanghai Synchrotron Radiation Facility (China). Multi-scan method

was used for absorption corrections. The structures were solved with direct method and were refined with SHELXL-2014.[S2]

Synthesis of $Ag_{51}(^{t}BuC{\equiv}C)_{32}Cl$

$^{t}BuC{\equiv}CAg$ (0.1133 g, 0.6 mmol) and dppp (1,3-bis(diphenyphosphino)propane, 0.2475 g, 0.6 mmol) were dissolved in 50 mL of methanol and dichloromethane (1:1) under vigorous stirring. A freshly prepared solution of $NaBH_4$ (0.9 mmol in 5 mL methanol) was added. The solution changed from colorless to yellow. After adding 0.5 mL Et_3N solution of $(Me_4N)Cl$ (0.0045 g, 0.039 mmol) and $^{t}BuPO_3H_2$ (0.008 g, 0.058 mmol), the reaction was aged for 15 h at ambient conditions, during which the color further turned dark black green. The mixture was centrifuged for 5 min at 7500 r/min. Slow evaporation of the dark solution afforded the product as black block crystals after one week. Yield: ca. 27% (based on $^{t}BuC{\equiv}CAg$). Elemental analysis (%) calcd for $C_{192}H_{288}ClAg_{51}$: C 28.35, H 3.57; found: C 28.64, H 3.91. IR (KBr, cm^{-1}): 2055 (C≡C).

Figure S1. The image of **Ag_{51}** (black block) under an optical microscope.

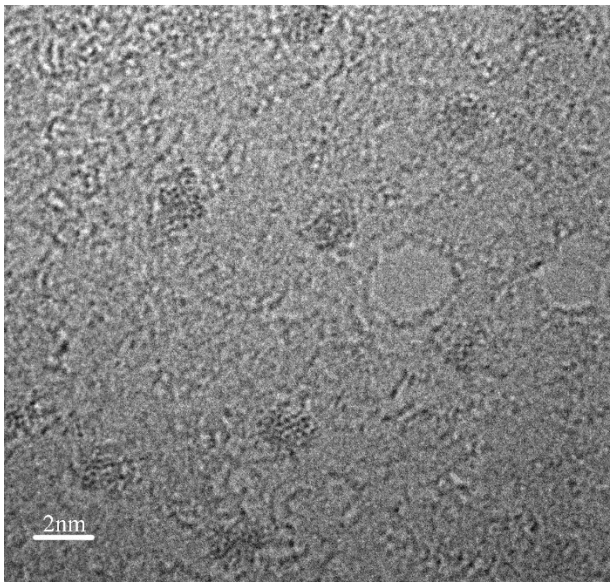

Figure S2. HR-TEM micrograph of $\mathbf{Ag_{51}}$.

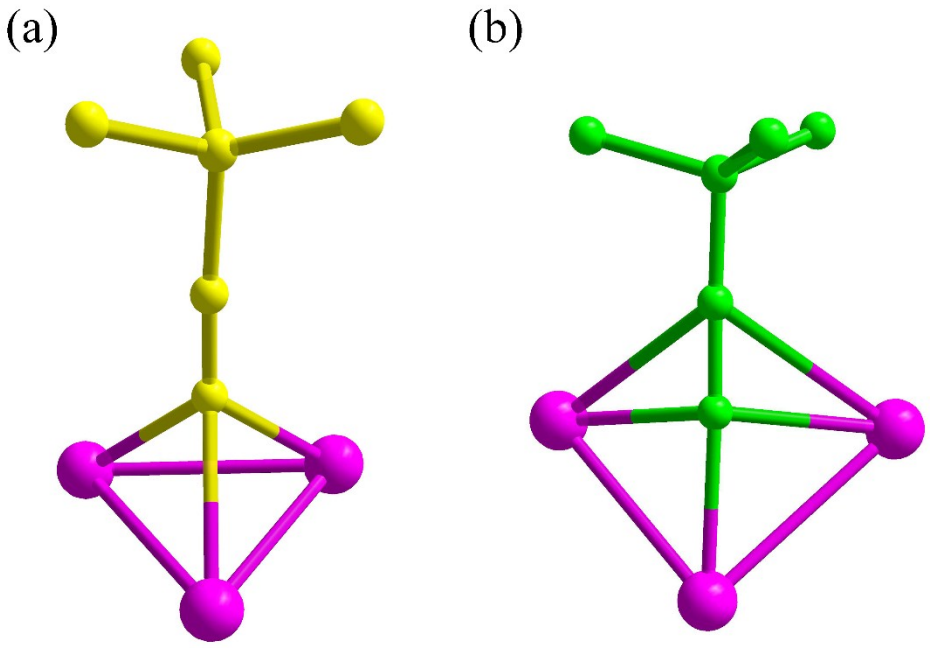

Figure S3. Illustration of bonding motifs of ^{t}BuC≡C^{-} ligands. (a) Type A. (b) Type B. Color legend: Ag, pink, light blue, dark blue, brown; C, yellow and green.

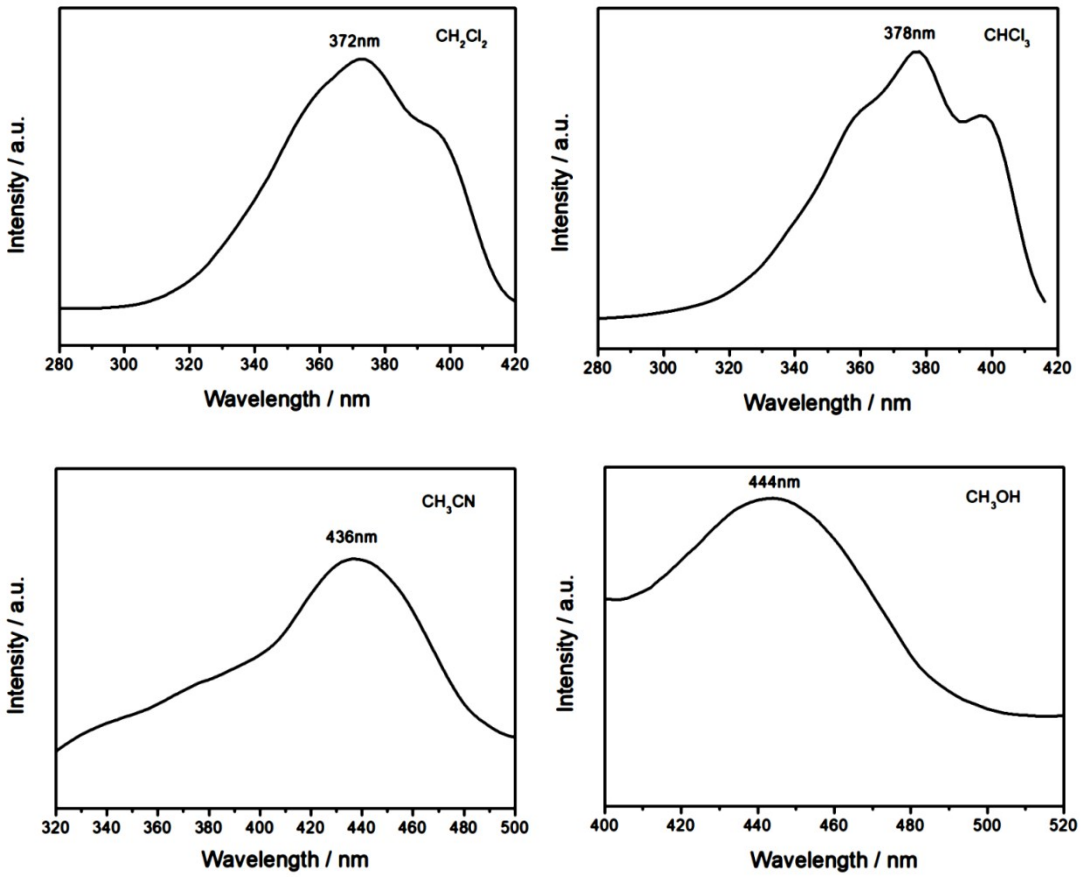

Figure S4. Excitation spectrum of $\mathbf{Ag_{51}}$ dissolved in CH_2Cl_2, $CHCl_3$, CH_3CN and CH_3OH.

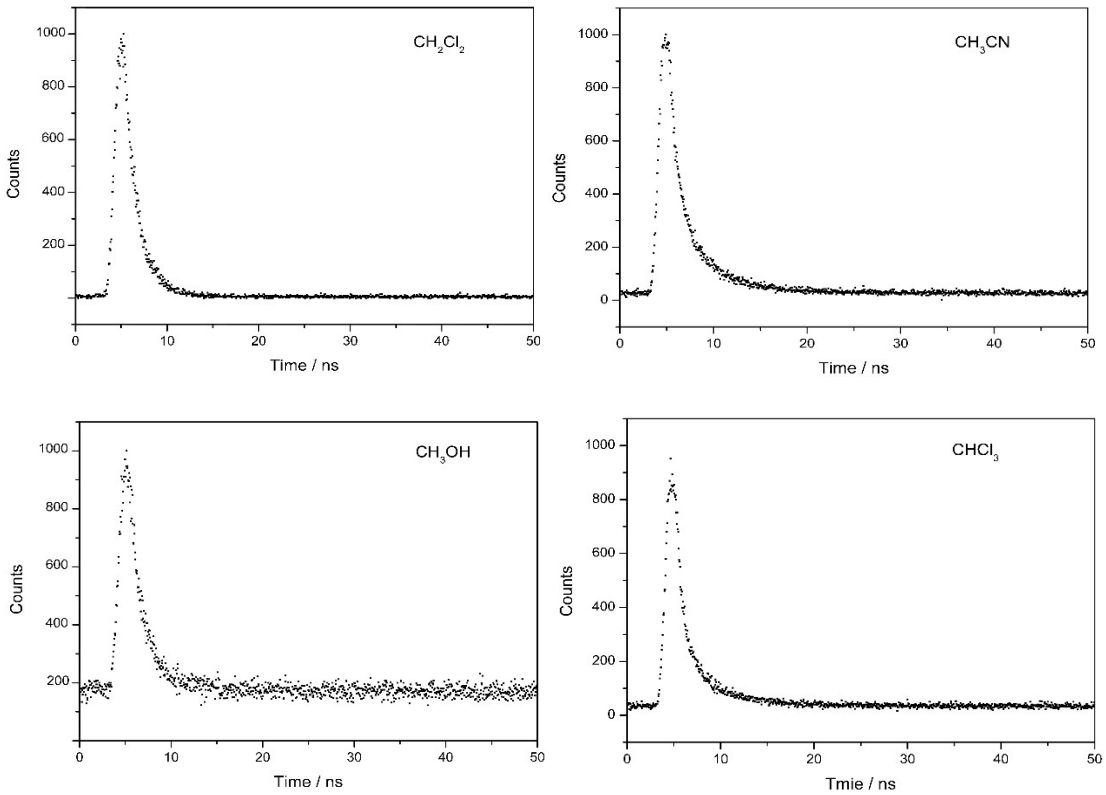

Figure S5. Fluorescence decay curves of **Ag_{51}** dissolved in CH_3OH, CH_3CN, $CHCl_3$ and CH_2Cl_2 at room temperature.

Table 1. The emission wavelengths and fluorescence lifetimes of **Ag_{51}** dissolved in different solutions.

Solution	λ_{em} (nm)	τ (ns)
CH_3OH	656	1.63
CH_3CN	570	1.87
$CHCl_3$	413, 437 and 469	1.51
CH_2Cl_2	418, 436 and 466	1.47

Table 2. Crystal data and structure refinement for $\mathbf{Ag_{51}}$

Empirical formula	$C_{192}H_{288}ClAg_{51}$
Formula weight	8133.07
Crystal system	Triclinic
Space group	*P-1*
a	19.438(1) Å
b	19.512(1) Å
c	19.537(1) Å
α	100.446(2)°
β	113.716(2)°
γ	102.272(2)°
V	6327.2(7) $Å^3$
Z	1
ρ_{calc}	2.127 Mg/m^{-3}
Absorption coefficient	3.036 mm^{-1}
F(000)	3841
Crystal size	0.32 x 0.24 x 0.16 mm^3
Crystal color and habit	black block
Theta range for data collection	2.049 to 24.742
Index ranges	-22<=h<=22, -22<=k<=22, -22<=l<=2
Reflections collected	78441
Independent reflections	20535 [*R*(int) = 0.0391]
Observed reflections (*I* > 2sigma(I))	16771
Goodness-of-fit on F^2	1.043
Final R indices [*I* > 2sigma(I)]	*R*1 = 0.1317, *wR*2 = 0.3092
R indices (all data)	*R*1 = 0.1573, *wR*2 = 0.3323
Largest diff. peak and hole	6.046 and -4.700 $eÅ^{-3}$
CCDC number	1857040

References

(S1) Jiang, Z.-G.; Shi, K.; Lin Y.-M.; Wang, Q.-M. *Chem. Commun.* **2014**, *50*, 2353.

(S2) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.