Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

The interesting luminescence behavior and rare nonlinear optical property of the $\{Ag_{55}Mo_6\}$ nanocluster

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1. Experimental

Optical measurement

Luminescence property of the $\{Ag_{55}Mo_6\}$ nanocluster in the solid state was investigated by an F-4500 fluorescence (FL) spectrophotometer combined with fluorescence lifetime and steady state spectrometer FLSP920.

The UV-Vis absorption spectroscopy was measured with a 752 PC UV/Vis spectrophotometer.

The NLO property of the $\{Ag_{55}Mo_6\}$ nanocluster in CH_3OH solution was evaluated by Z-scan technique using an optical parametric amplifier (ORPHEUS, Light Conversion) which generated 190 fs laser pulses at 400 nm with repetition rate of 20 Hz. The experimental setup was similar to the one in Ref 1. The titled sample was poured into a quartz cell with a thickness of 2 mm, placed at the focal point of a lens with a focal length of 40 cm, and moved along the axis of the incident beam (z direction). The open-aperture and closed-aperture measurements were carried out with the input energy of 13 nJ. The incident and transmitted laser pulses were monitored by utilizing two energy detectors (Rjp-765 energy probes, Laser Precision), which were linked to an energy meter (Rj-7620 Energy Ratiometer, Laser Probe Inc.). A computer was used to process the data coming from the energy meter via a GPIB interface.

Method of calculation

Singlet-point calculation was carried out using B3LYP functional, 3-21G basis set for non-metal atoms and LAND2DZ basis set for Ag and Mo atoms in Gaussian 16 program package.[2,3] And the molecular orbital (MO) calculations of the $[Ag_{55}(MoO_4)_6(C{\equiv}C^tBu)_{24}(CH_3COO)_{18}]^+$ cluster skeleton in the $\{Ag_{55}Mo_6\}$ nanocluster were completed in Multifwn software.[4]

2. Physical Measurements

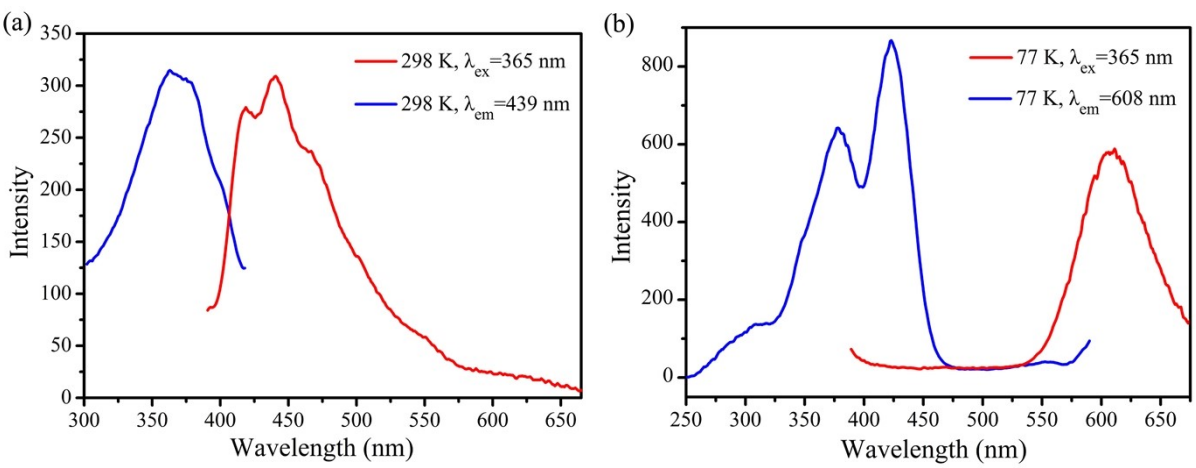

Fig. S1 The excitation and emission spectra of **1** at 298 K (a) and 77 K (b) upon excitation at 365 nm measured on an F-4500 Fluorescence (FL) Spectrophotometer.

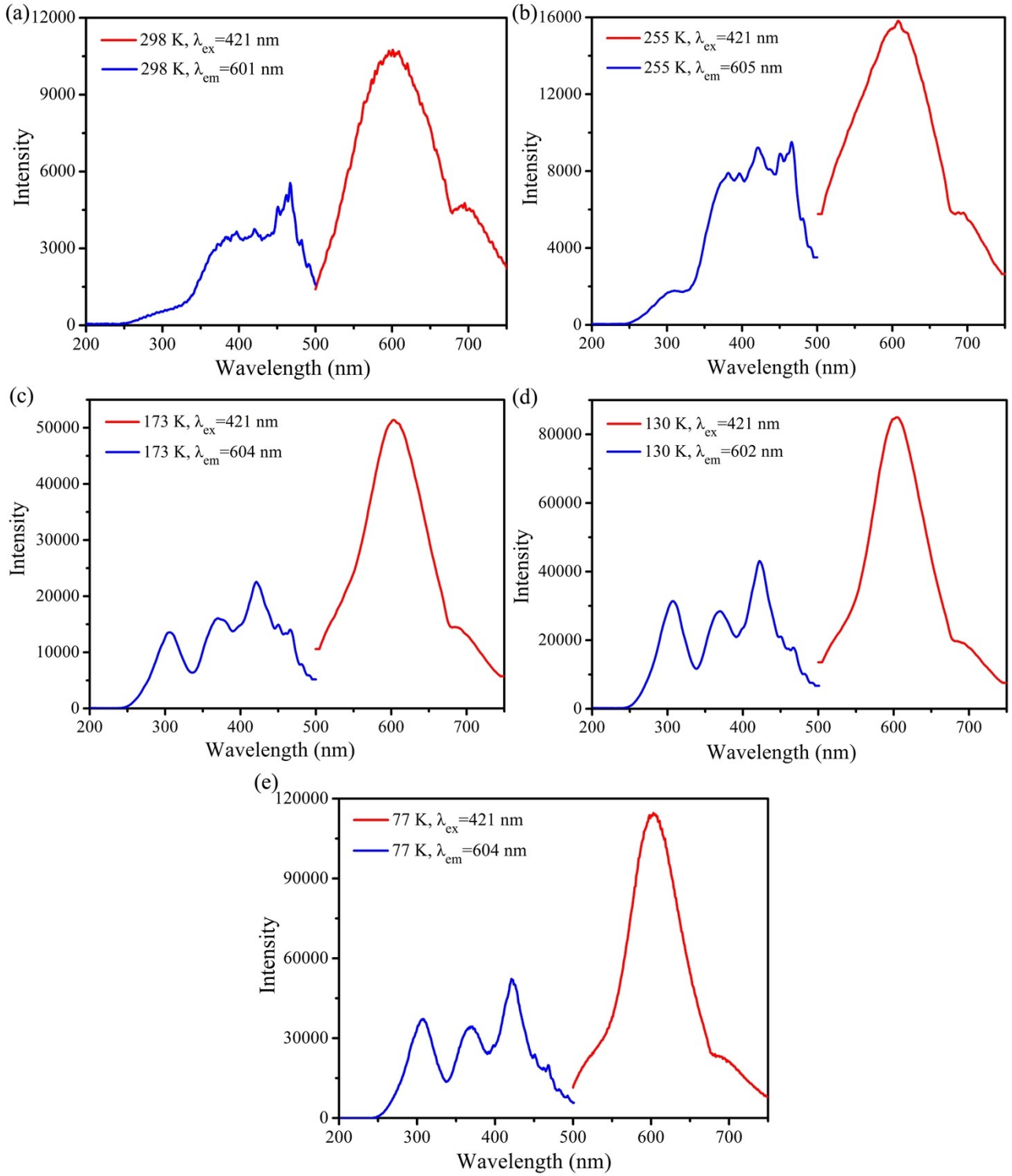

Fig. S2 The excitation and emission spectra of **1** at 298 K (a), 255 K (b), 173 K (c), 130 K (d) and 77 K (e) upon excitation at 421 nm measured on a Combined Fluorescence Lifetime and Steady State Spectrometer FLSP920.

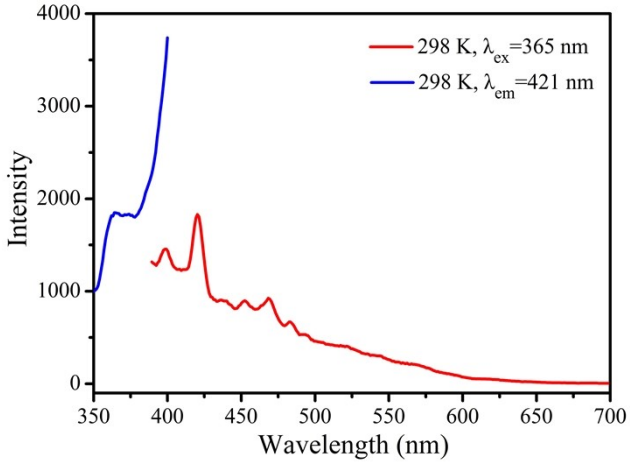

Fig. S3 The excitation and emission spectra of AgC≡C^{t}Bu ligand at 298 K upon excitation at 365 nm measured on an F-4500 Fluorescence (FL) Spectrophotometer.

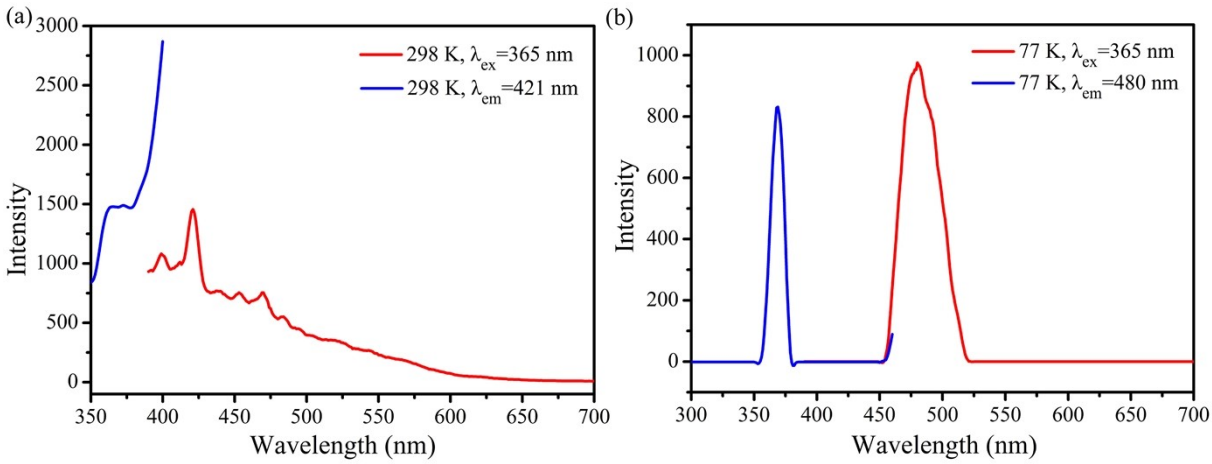

Fig. S4 The excitation and emission spectra of the mixture of the initial reaction materials at 298 K (a) and 77 K (b) upon excitation at 365 nm measured on an F-4500 Fluorescence (FL) Spectrophotometer.

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