Supporting Information

Ultrafast Intersystem Crossing in Isolated $Ag_{29}(BDT)_{12}^{3-}$ Probed by Time-Resolved Pump-Probe Photoelectron Spectroscopy

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A. Details of Experimental Methods: Pump-Probe Photoelectron Spectroscopy

A schematic of the setup used is shown in figure S1. Ions were generated with a nano-ESI source. The glass needles used were 5 cm long with a tip diameter of a few µm and a capacity of ca. 50 µl. The spray voltage was between 7 and 8 kV. Ions were transferred through a 20 cm long and resistively heated capillary into the first vacuum chamber with a pressure of 1 mbar. There the ions are focused and guided to the TOF mass spectrometer with an ion funnel. The last electrode of the funnel was pulsed with a higher potential to trap and accumulate ions before being released into the TOF mass spectrometer. Ions were then accelerated to 4 kV by pulsed Wiley-McLaren acceleration grids (1 kHz, 15 µs) into a 3 m long flight tube and then detected with an MCP. The mass spectrometer has a mass resolution of 200 m/Δm. The ion beam is collimated with Einzel lenses and steered with deflection plates immediately after the acceleration region.

The perpendicularly oriented VMI photoelectron spectrometer is located 15 cm before the TOF ion detector. Three acceleration electrodes made of 1 mm thick stainless steel plates and a diameter of 7.75 cm are arranged in an Eppink-Parker like setup. They are mounted on insolating ceramic rods and separated by 12.7 mm with ceramic spacers. To avoid deflecting the ions prior to photodetachment, the voltages of the VMI setup (-5 kV for the repeller and -3.45 kV for the extractor at 1 kHz) were only applied for 200 ns coinciding with the interaction of the laser with the ions. The photoelectron cloud is accelerated through holes in the extractor and ground plate, 15 mm and 20 mm respectively towards the detector through the 60 cm long electron flight tube. The detector is composed of a position sensitive MCP, phosphor screen and CCD camera. The impact of an electron is then recorded by a high resolution CCD-camera with a repetition rate of 32 Hz. Thus ca. 31 laser shots are recorded in 1 image. For reconstruction of the convoluted image, a polar onion peeling algorithm from the Verlet-group is used.

The femtosecond laser system used (Astrella, Coherent) operates at 1 kHz and provides 34 fs pulses with 7 mJ pulse energies at 800 nm. UV and 490 nm pulses were generated by a TOPAS Prime (Light conversion). The TOPAS is pumped with 800 nm (3 mJ) and generates an output energy of 100 µJ at 490 nm and ca. 10 µJ in the UV-region. All pulses enter the spectrometer unfocused with a beam diameter of ca. 6 mm through a 3 mm thick CaF_2-window.

For the pump-probe experiment the 490 nm laser beam (100 uJ) was aligned collinearly with the fundamental 800 nm beam (400 µJ) by a dichroic combiner mirror. The variable delay times were realized by a computer controlled delay stage. The 490 nm radiation was perpendicularly polarized relative to the ion beam direction. To change the polarization between pump and probe pulse, a λ/2 waveplate (800 nm, mica, B. Halle Nachfl. GmbH) was used. For the power dependency, measurements the laser intensity was controlled by a 1 mm thick variable metallic neutral density filter.

Both, pump and probe pulses, are assumed to have a Gaussian beam shape with a diameter of 6 mm. The ions are focused by an Einzel lens through a 5 mm hole into the VMI setup. Thus, the laser beam is slightly bigger than the ion cloud. The laser is aligned to get maximal electron signal.

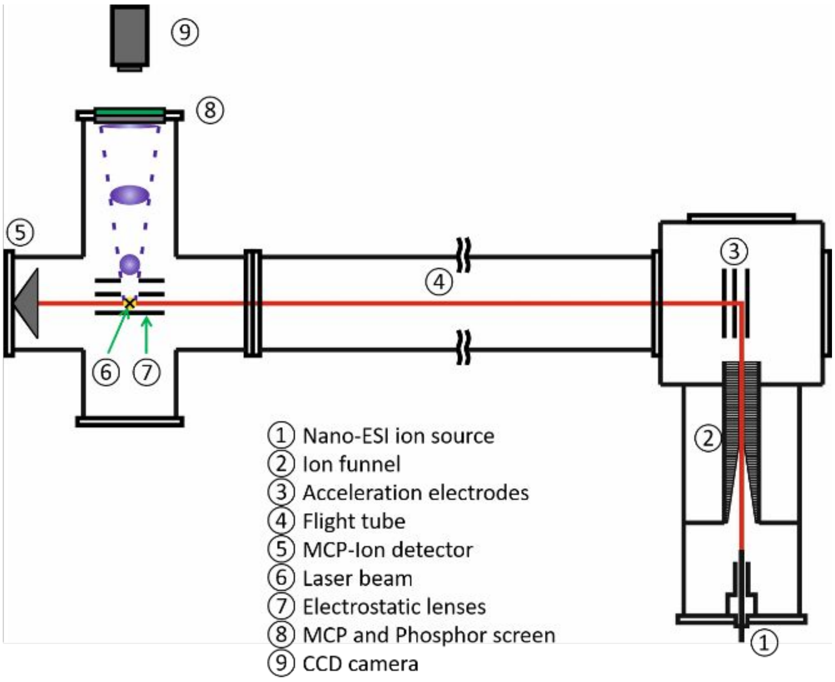

Figure S1. Schematic diagram (not to scale) of the apparatus used in the current experiments

B. DFT Calculations

$Ag_{29}(BDT)_{12}^{3-}$ geometries were obtained from DFT calculations with the BP-86 functional and the def-SV(P) basis set as implemented in the TURBOMOLE package.[50] We used the experimental geometry (X-ray structure) of $Ag_{29}(BDT)_{12}(TPP)_4$ as the starting point and removed the four TPP neutral phosphine ligands to obtain a $Ag_{29}(BDT)_{12}^{3-}$ structure which was taken as the starting for geometry optimization without any symmetry restrictions.

C. Condensed phase spectroscopy of $Ag_{29}(BDT)_{12}(TPP)_4$

(a) The electronic absorption spectrum in DMF solution was taken using a Varian Cary 500 UV-Vis-NIR spectrophotometer at room temperature. The spectrum was measured in the range of 250-800 nm with 1 nm resolution.

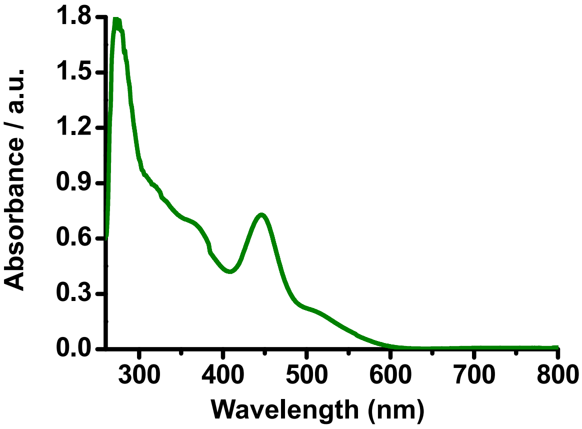

Figure S2. Electronic absorption spectrum of $Ag_{29}(BDT)_{12}(TPP)_4$ in DMF solution

(b) Photoluminescence measurements were performed on a Horiba Jobin Yvon Fluorolog-322 spectrometer equipped with a closed-cycle optical cryostat operating within a temperature range of 15-300 K. A Hamamatsu R9910 photomultiplier was used as detector for the emission spectral range of ~300-850 nm. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). A solid sample (crystalline powder) of $Ag_{29}(BDT)_{12}(TPP)_4$ was measured dispersed in a thin layer of viscous perfluorocarbon oil between two 1 mm quartz plates. This sample holder was mounted on the cold finger of the cryostat. PL decay traces was recorded by connecting the photomultiplier to a 500 MHz LeCroy LT322 oscilloscope (via a 50 or 500 Ω load depending on the decay time scale) and using a nitrogen laser (~2 ns, ~5 μJ per pulse) for pulsed excitation at 337 nm. The PL quantum yield of crystalline $Ag_{29}(BDT)_{12}(TPP)_4$ at ambient temperature was determined using an integrating sphere which was installed into the sample chamber of the spectrometer. The uncertainty of this measurement was estimated to be ±10 %.

Figure S3 shows PL emission and excitation (PLE) spectra of $Ag_{29}(BDT)_{12}(TPP)_4$ in a DMF solution (saturated with argon gas) and in the solid state. In room temperature DMF, the cluster emits relatively weak PL with a maximum at ca. 670 nm (1.85 eV) and a lifetime of 70 ns. In contrast, the solid compound demonstrates a bright, broad NIR emission at ca. 770 nm (1.61 eV) with a quantum yield of 11 % (excitation at 450 nm). At low temperatures, the emission band shifts to ca. 740 nm (1.68 eV) and increases in efficiency up to 40 % as estimated from the temperature-dependent PL spectra (Figure S3). The PL decay of solid $Ag_{29}(BDT)_{12}(TPP)_4$ follows biexponential curves with the following times and relative weights: $\tau_1 =$ 31 μs (45%) and $\tau_2 =$ 130 μs (55%) at T = 17 K and τ_1 = 1.0 μs (57%) and τ_2 = 5.3 μs (43%) at T = 295 K. The relatively slow decay clearly indicates that the emission of the silver cluster is phosphorescence.

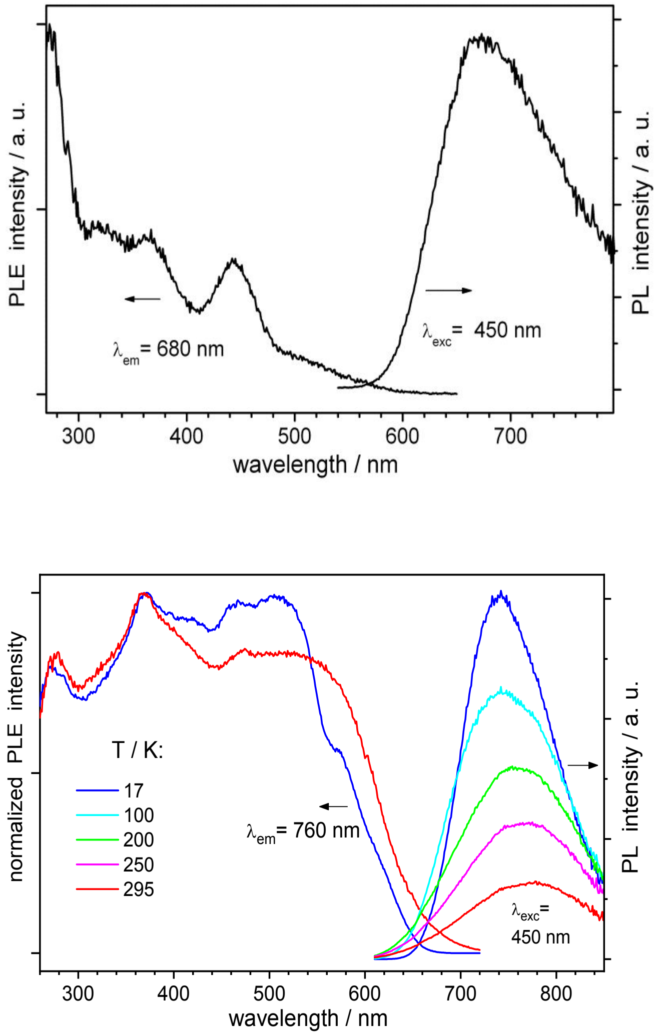

Figure S3. Photoluminescence emission (PL) and excitation (PLE) spectra for $Ag_{29}(BDT)_{12}(TPP)_4$ dissolved in DMF and measured at room temperature and as a solid (polycrystalline) sample at various temperatures between 17 and 295 K (top and bottom panels, respectively). Note, that at room temperature for an excitation wavelength of 450 nm, the maximum of the solid photoluminescence spectrum is observed at ca. 770 nm (1.61 eV) whereas in DMF solution it is seen at ca. 670 nm. By comparison, Bakr et al.[17] report an emission maximum of 670 nm (1.85 eV) in solution and at 715 nm (1.73 eV) for the solid – both measurements presumably carried out at room temperature.

D. Glotaran global analysis of tr-PES measurements

Glotaran (**Glo**bal and **tar**get **an**alysis) is a software package specially designed for analysis of data obtained by time-resolved spectroscopy. It allows users to analyze the whole data set at once with a user-given kinetic model, i.e. a series of sequential decays or parallel decays. The model used here is a Gaussian type instrument response function (IRF) and a sequence of three exponential decays corresponding to the observable states: (i) the first excited CT-states; (ii) the "doorway" state for ISC; (iii) the long-living triplet-state.

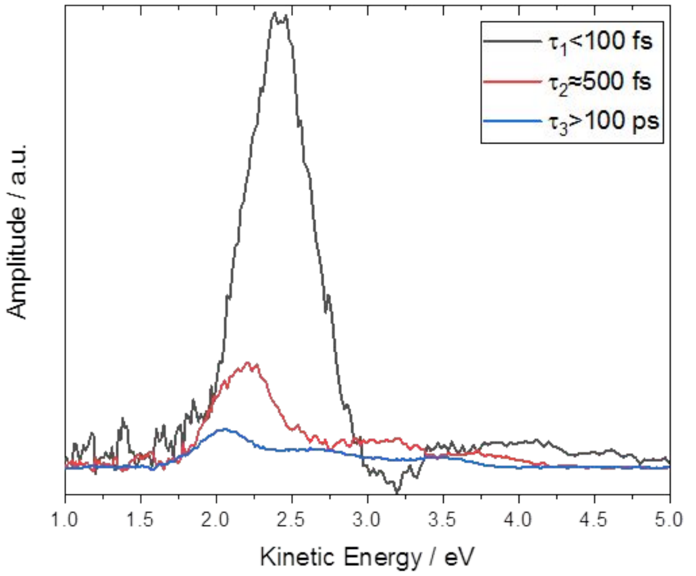

Figure S4. Glotaran global analysis of the 490 /800 nm pump-probe transient measurements (parallel polarization) shown in the contour plot of Fig. 4. The analysis assumes sequential kinetics: fast decay to an intermediate state followed by fast decay to a long lived state. This results in best fitting unimolecular decay rates of >10, ~2 and <0.01 ps^{-1} respectively. Shown are resulting decay associated difference spectra which correspond roughly to the PE spectra of the initially populated (black), the intermediate (red) and the long-lived state (blue) which we assign as a triplet.

E. Final (dianion) state energetics

The one-color measurements of Figure 3 indicate that interaction with two photons (490 nm, 2.53 eV) leads to two resolvable detachment features. The higher EKE singlet detachment feature at 3.41 eV implies that ca. 0.65 eV of excess energy (2 x 2.53 – 1 – 3.41 = 0.65 eV) must be going into final state vibrational excitation. We have rationalized the lower EKE feature at 2.66 eV as corresponding to triplet detachment within the same laser pulse, i.e, a comparable inelasticity of ca. 0.4 eV must pertain (1.53 + 2.53 – 1 - 2.66 = = 0.4 eV). Note further, that in the one-color measurement the triplet feature is significantly more intense than the singlet component. By contrast, the triplet is much weaker than the singlet signal in the pump-probe measurement. Presumably, this reflects the RCB barrier height which at 2.6 ± 0.2 eV (as measured from the trianion ground state) is comparable to the sum of triplet state and probe pulse energies (1.53 + 1.55 = 3.06 eV). Therefore, the relative triplet detachment cross section is expected to be much higher at the 490 nm pump photon wavelength.