Supplementary Information

A. Quantum Yield and Energy Transfer Rate for Ag_{15} and Ag_{32}

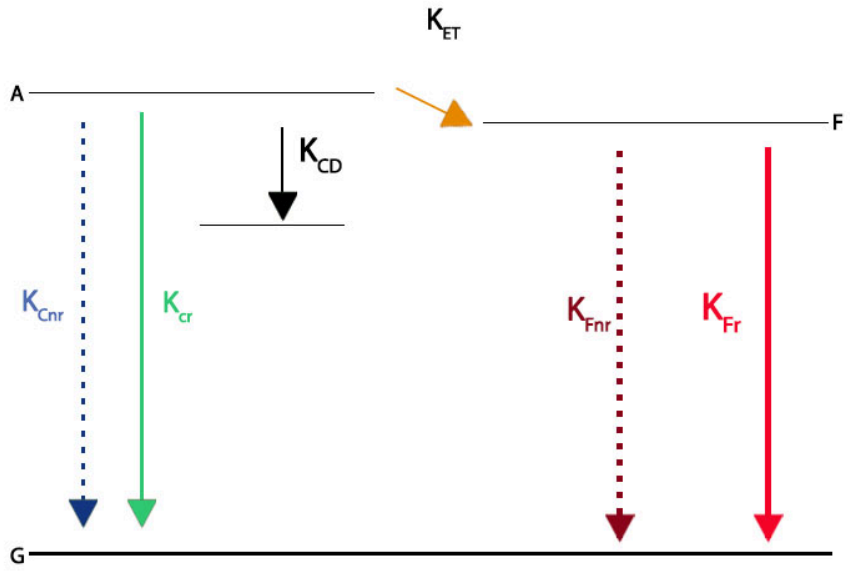

Figure S1. Energy transfer model

After excitation by the laser pulse, N_o is the initial amount of excited population in the A state. The relaxation from the A state to the F state (the population of the F state as N_F) can be calculated by the product of the initial population, the rate of energy transfer into the emissive state (K_{EET} or K_{ET}) and the lifetime of level C (τ_c) can be described as:

$$N_F = N_A \cdot K_{EET} \cdot \tau_{CT} \qquad (1)$$

For state A , the total transfer rate of state A (K_{AT}) is the sum of the non-radiative rate (nr), the radiative rate (r) and the “dark state” (d) defined as:

$$K_{AT} = K_{Cnr} + K_{Cr} + K_{CD} \qquad (2)$$

And K_{AT} can be defined in terms of τ_A:

$$K_{AT} = 1/\tau_A \qquad (3)$$

The N_F can be rewritten using equation 1, 2 and 3 as:

$$N_F = N_A \cdot K_{EET}/K_{AT} \qquad (4)$$

As no fast component is detected in the ground state bleach, we can assume that $K_{Cnr}+K_{Cr} << K_{CD.}$ We also suggested that the energy transfer rate (K_{EET}) is smaller than K_{CD} which is in the fs range for Ag_{32}.

Considering the fact that not all of N_F is emissive, we can consider the number of fluorescence photons (n_p) emitted from state F as the product of the population of the emissive state and the portion of the radiative decay rate (K_{Fr}) and total decay rate (K_{FT}) :

$$n_p = N_F \cdot K_{Fr}/K_{FT} \qquad (5)$$

K_{FT} is defined as the sum of the radiative (K_{Fr}) and non-radiative rates (K_{Fnr}) similar to how K_{AT} is defined in equation (2) without the "dark state".

$$K_{FT} = K_{Fnr}+K_{Fr} \quad (6)$$

Combining equation 5 and equation 4 we can generalize Np to be:

$$n_p = N_A \cdot K_{EET} \cdot K_{Fr} \cdot 1/K_{AT} \cdot 1/K_{FT} \qquad (7)$$

To fully understand K_{EET}, the quantum yield of the system can be used. The fluorescence quantum yield (Q.Y.) is defined by the number of emitted photons per one absorbed excitation photon, which can be defined with equation (7) as:

$$Q.Y. = n_p/N_A = K_{EET} \cdot K_{Fr} \cdot 1/K_{AT} \cdot 1/K_{FT} \text{ or } Q.Y. = n_p/N_A = K_{EET} \cdot K_{Fr} \cdot \tau_{AT} \cdot \tau_{FT} \qquad (8)$$

For the case of Ag_{15}, using a Q.Y of 0.029 and τ_{AT} is 3 ps and τ_{FT} is 130 ps, the K_{EET} is calculated to be $1/K_{Fr} \cdot 7.4 \cdot 10^{19} s^{-1}$.

The relation of K_{EET} and K_{Fr} is illustrated in equation 6, which can be rewritten to give the inequality equation (9). Using the inequality (9), K_{EET} for Ag_{15} is estimated to be $\geq 9.7 \cdot 10^{9} s^{-1}$ or a τ_{EET} of $\leq$ 103 ps.

$$K_{Fr} = 1/\tau_{FT} - K_{Fnr} (7) \text{ or } K_{Fr} \leq 1/130 \text{ ps} \quad (9)$$

Using the same calculation for Ag_{32} and assume that K_{FT} for Ag_{32} is the same as K_{FT} (130ps), the resulting energy transfer rate $K_{EET} = 1.67 \cdot 10^{10} s^{-1}$ or τ_{EET} of $\leq$ 60 ps. The K_{EET} for Ag_{15} is 1.7 times that of Ag_{32}. Considering experiment uncertainty and fitting errors, it is reasonable to consider that Ag_{32} and Ag_{15} have the same K_{EET}, which suggests that they have structural similarities which affect the emission mechanism.

B. $Ag_{32}(SH)_{20}^{6-}$ Model Cartesian Coordinates in Angstroms

Ag	-0.032034	-1.470129	2.249637
Ag	-2.276593	0.058349	1.437332
Ag	-2.367855	0.107761	-1.377183
Ag	-0.121327	-1.373848	-2.289680
Ag	1.303896	-2.381089	-0.040176
Ag	-1.569206	-2.277476	-0.044068
Ag	-0.202029	-4.236911	1.621351
Ag	-2.613778	-2.478760	2.544598
Ag	-4.335709	-1.391616	0.134449
Ag	-2.687321	-2.497321	-2.693529

Ag	-0.214596	-4.162275	-1.748182
Ag	2.513496	-2.738826	2.527621
Ag	4.121716	-1.820174	-0.128544
Ag	2.371374	-2.616631	-2.602670
Ag	1.497493	0.004516	-4.138267
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H	0.312371	-3.437683	4.449264
S	-3.725580	-4.484744	3.285900
H	-2.795136	-5.282404	2.680196
S	-4.974189	-2.962361	-1.730906
H	-4.548825	-4.107995	-1.124789
S	-1.162196	-3.989615	-4.140936
H	-0.323182	-2.993499	-4.559322
S	-0.675721	-6.026444	-0.091030
H	-2.020396	-5.811156	-0.173293
S	4.856823	-3.353620	1.747447
H	4.422842	-4.527901	1.207155
S	5.653119	-0.301678	-1.508173
H	6.792575	-0.347741	-0.754377
S	4.149951	-3.702516	-3.836029
H	5.040577	-2.760434	-3.404198
S	2.290845	-1.070042	-6.153543
H	2.972167	-2.016689	-5.416458
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C. Density of states of $Ag_{15}(SCH_3)_{11}$

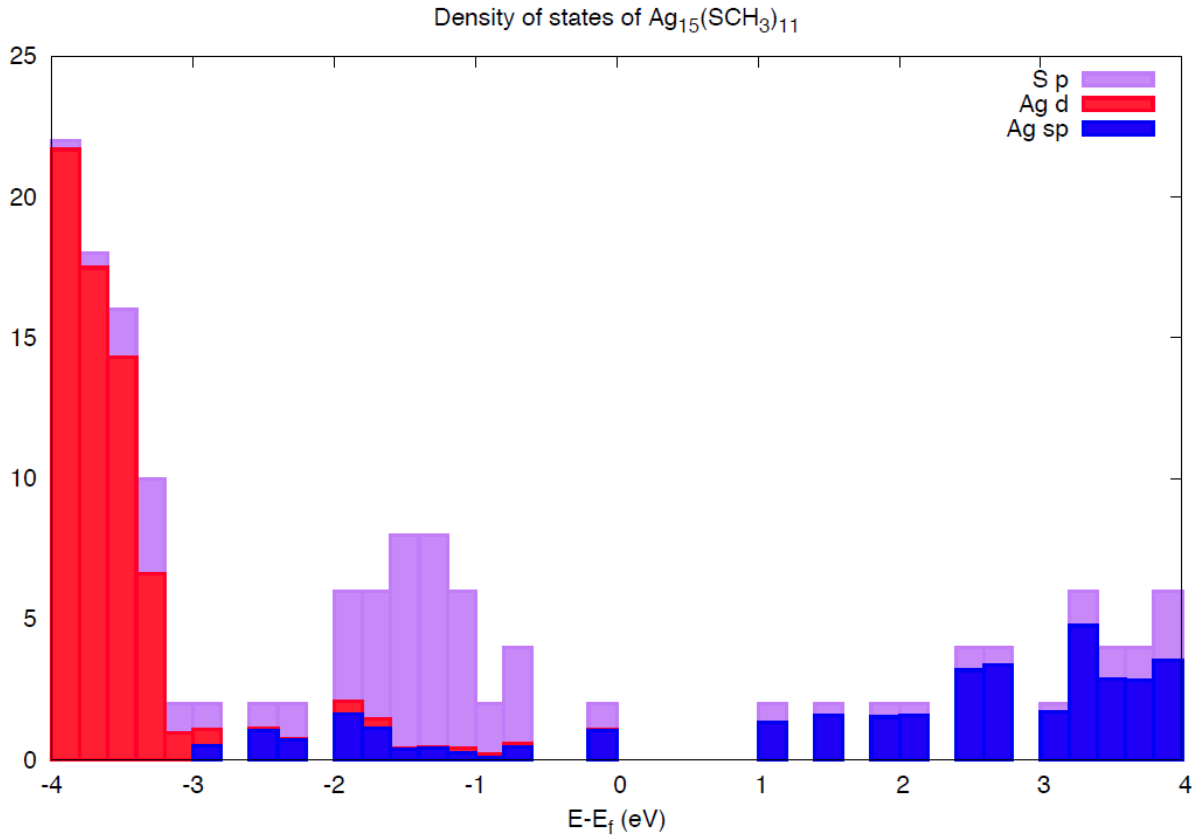

Figure S2. Density of states of $Ag_{15}(SCH_3)_{11}$ as calculated by DFT

D. Density of states of $Ag_{32}(SH)_{20}^{6-}$"

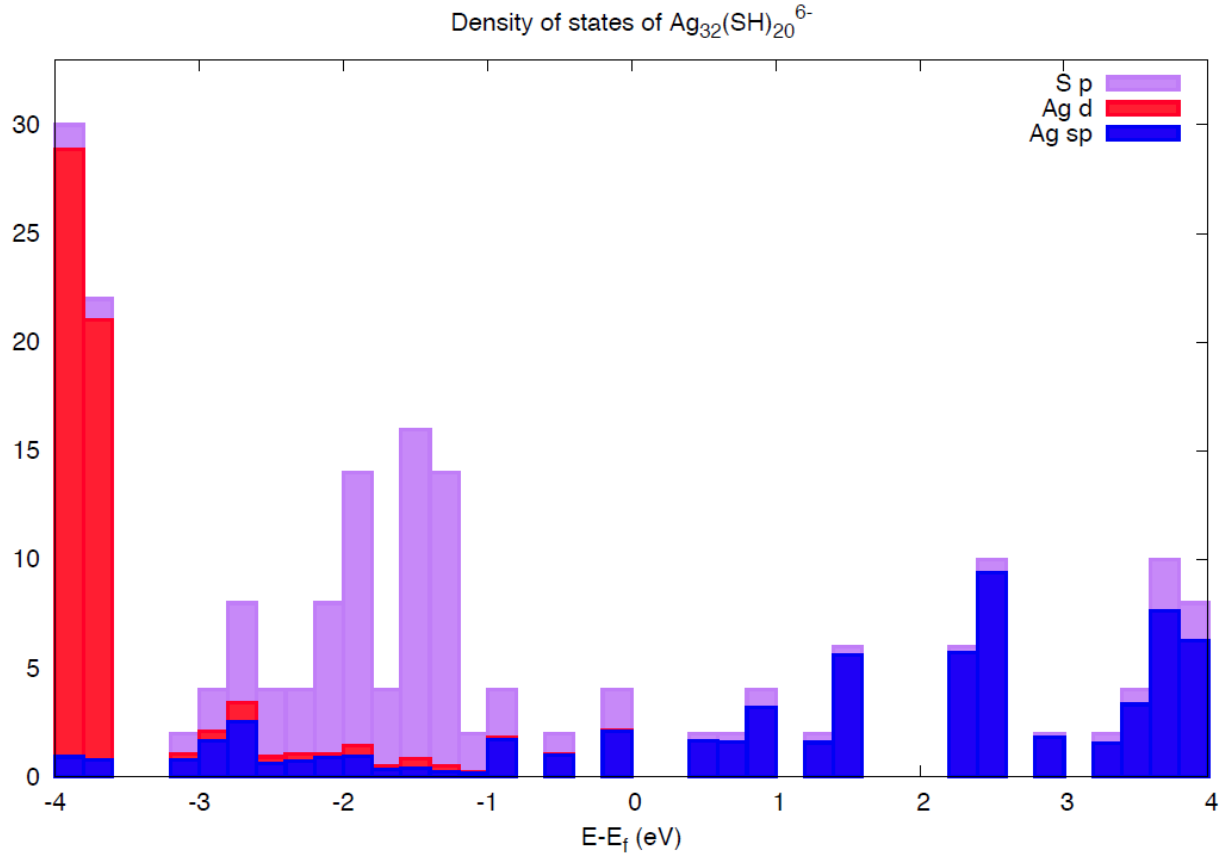

Figure S3. Density of state of $Ag_{32}(SH)_{20}^{6-}$ as calculated by DFT