Inter-cluster electron transfer $X^{2-} + X^0 \rightarrow 2X^-$ (X = $PtAu_{24}(SC_nH_{2n+1})_{18}$): effect of alkyl chain length of thiolate ligands on reaction rate

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It has been thought that metal clusters protected by ligands retain their identity as distinct entities even in the presence of other clusters. However, recent studies have revealed their dynamic nature in solution, where they exchange constituent metals and ligands.[1,2] We have recently found that $[PtAu_{24}(SC_2H_4Ph)_{18}]^-$ (denoted as X^-) having an icosahedral $Pt@Au_{12}(7e)$ core was spontaneously formed via electron transfer (ET) from $[PtAu_{24}(SC_2H_4Ph)_{18}]^{2-}$ (X^{2-}) to $[PtAu_{24}(SC_2H_4Ph)_{18}]^0$ (X^0) with $Pt@Au_{12}(6e)$ and $Pt@Au_{12}(8e)$ cores, respectively (Fig. 1):[3] $X^{2-} + X^0 \rightarrow 2X^-$. In this study, we systematically determined the ET rates (k_{ET}) from $[PtAu_{24}(SC_nH_{2n+1})_{18}]^{2-}$ (X_n^{2-}) to $[PtAu_{24}(SC_mH_{2m+1})_{18}]^0$ (X_m^0) with n, m = 2–16.

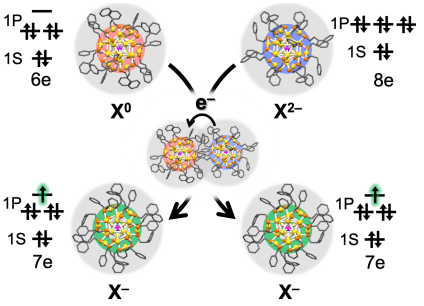

Fig. 1. Inter-cluster ET reaction from X^{2-} to X^0 (X = $PtAu_{24}(SC_2H_4Ph)_{18}$).

Figure 2 shows the k_{ET} values for $X_n^{2-} + X_m^0 \rightarrow X_n^- + X_m^-$ determined by analyzing time dependent UV-Vis absorption spectra of the mixture of X_n^{2-} and X_m^0. The k_{ET} values decreased with increase in the n+m values in the range of 4–12, but increased in the range of 12–32. The former behavior can be explained in such a manner that the overlap of the superatomic orbitals required for ET is hindered by longer alkyl chains. In contrast, the latter counterintuitive behavior implies that the overlap of the superatomic orbitals is promoted due to the formation of long-lived dimer by vdW interaction between the alkyl chain. This hypothesis was supported by the observation of $(X_n \cdot X_m)^{2-}$ by electrospray ionization mass spectrometry of the mixture of X_n^{2-} and X_m^0.

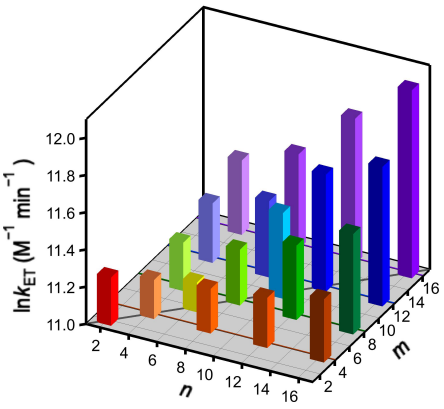

Fig. 2. ET rate constants as a function of (n, m).

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