First-principles study on charge-transfer in actinide-containing superatom from surface-enhanced Raman scattering

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Part 1. Functionals, basis set, and calculated relative energies for different multiplicities of (An@Ag$_{14}$, An = Ac$^-$, Th, Pa$^+$).

Table S1. Relative bonding energies calculations for An@Ag$_{14}$.

System	Functionals/Basis set	Multiplicity	$\triangle$E (eV)
Th@Ag$_{14}$	BP86/TZP	**1**	**0.00**
		3	1.42
		5	2.97
	PBE/TZP	**1**	**0.00**
		3	1.49
		5	3.13
	PBE0/TZP (single-point)	**1**	**0.00**
		3	2.21
		5	4.48
[Ac@Ag$_{14}$]$^-$	BP86/TZP	**1**	**0.00**
		3	0.67
		5	1.81
[Pa@Ag$_{14}$]$^+$	BP86/TZP	**1**	**0.00**
		3	0.01
		5	1.45

Part 2. Computational details

For systems containing actinides or transition metal elements, the electron correlations can be handled effectively without significantly increasing the computational complexity in DFT calculations.[1-5] Therefore, the spin-polarized generalized gradient approximation (GGA) with the Becke-Perdew (BP86) exchange-correlation functional[6, 7] was used throughout this work. Both scalar relativistic (SR) and spin-orbit coupling effects (SOC) have been taken into account through zeroth order regular approximation (ZORA).[8-11] Moreover, we also used Perdew-Burke-Ernzerhof (PBE),[12] and hybrid Perdew-Burke-Ernzerhof (PBE0)[13] functionals to validate our calculation procedure. Since a full geometric optimization with the hybrid exchange-correlation functionals for Amsterdam Density Functional (ADF) package is computationally too demanding, we performed single-point energy calculations at the PBE0 level based on the BP86 geometry.[4, 14] A triple-ζ with polarization functions (TZP) uncontracted Slater-type orbital (STO) basis set was used,[15] with a $[1s^2\text{-}3d^{10}]$ frozen core for Ag, a $[1s^2\text{-}4f^{10}]$ frozen core for Th ,Ac, Pa and full electrons for N, C, and H atoms, respectively. All optimized structures thus obtained were analyzed with vibration frequency calculations at the same level to avoid imaginary frequencies.

The TDDFT method, which is based on a short-time approximation to the Raman scattering cross section, has been widely used in the theoretical study of SERS. This method not only can deal with the molecule and the metal at the same level of theory, but also can describe the different SERS enhancement mechanisms and their relation to other optical properties in a uniform way, thereby providing accurate microscopic insights into SERS. And its theoretical results for some closed-shell molecular systems are consistent with the experimental data.[16, 17] All calculations in this study have been done by employing the Amsterdam density functional (ADF) program.[18] Considerable researches have shown that the exchange correlation functional BP86[6, 7] is appropriate for describing electronic and optical properties of metal-molecule coupled systems, whether it is pure theory or the combination of the theoretical and experimental work.[16, 17, 19, 20] And BP86 functional usually gives harmonic frequencies close to experimental results without the use of scaling factors,[21] thereby it is used in this work.

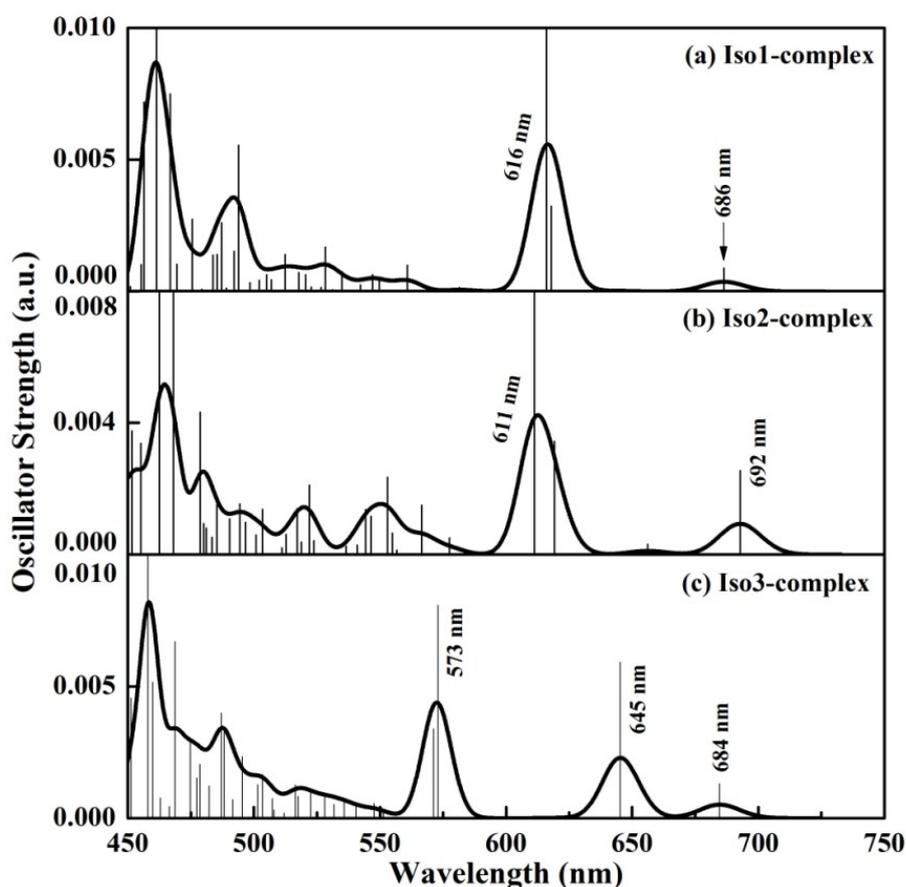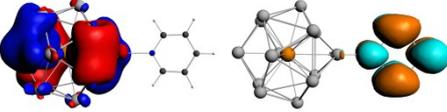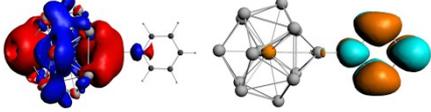**Part 3. Calculated absorption spectrum of three complexes at SAOP/TZP level.**
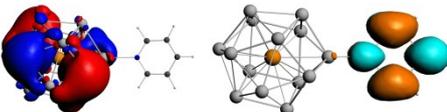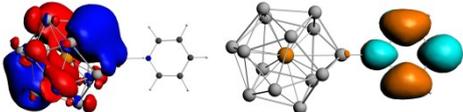

Figure S1. Absorption spectra of the three complexes at SAOP/TZP level.

Table S2. Calculated excitation energies (E in eV), excitation wavelengths (λ in nm), oscillator strengths (*f*) and orbital transitions of charge-transfer excitations for three complexes, respectively.

Geometry	E / λ	*f*	Transitions		weight
Iso1-complex	2.01 / 616	0.0103	1D → π*		0.9960
	1.81 / 686	0.0009	1D → π*		0.9980
Iso2-	2.03 / 611	0.0097	1D → π*		0.9020
			1D → π*		

complex	1.79 / 692	0.0026			0.9940
Iso3-complex			1D $\rightarrow$ π^*		
	2.16 / 573	0.0081			0.8700
			1D $\rightarrow$ π^*		
	1.92 / 645	0.0059			0.9920

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