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Three-atom-wide gold quantum rods with periodic elongation and strongly polarized excitons

Lianshun Luo[a,1], Zhongyu Liu[a,1], Jie Kong[b,1], Christopher G. Gianopoulos[c], Isabelle Coburn[a], Kristin Kirschbaum[c], Meng Zhou[b,2], and Rongchao Jin[a,2]

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[1]Department of Chemistry, Carnegie Mellon University, Pittsburgh PA 15213, USA.

[2]Hefei National Research Center for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China.

[3]Department of Chemistry and Biochemistry, University of Toledo, Toledo, Ohio 43606, USA.

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Paper Presentation

Sooraj B S

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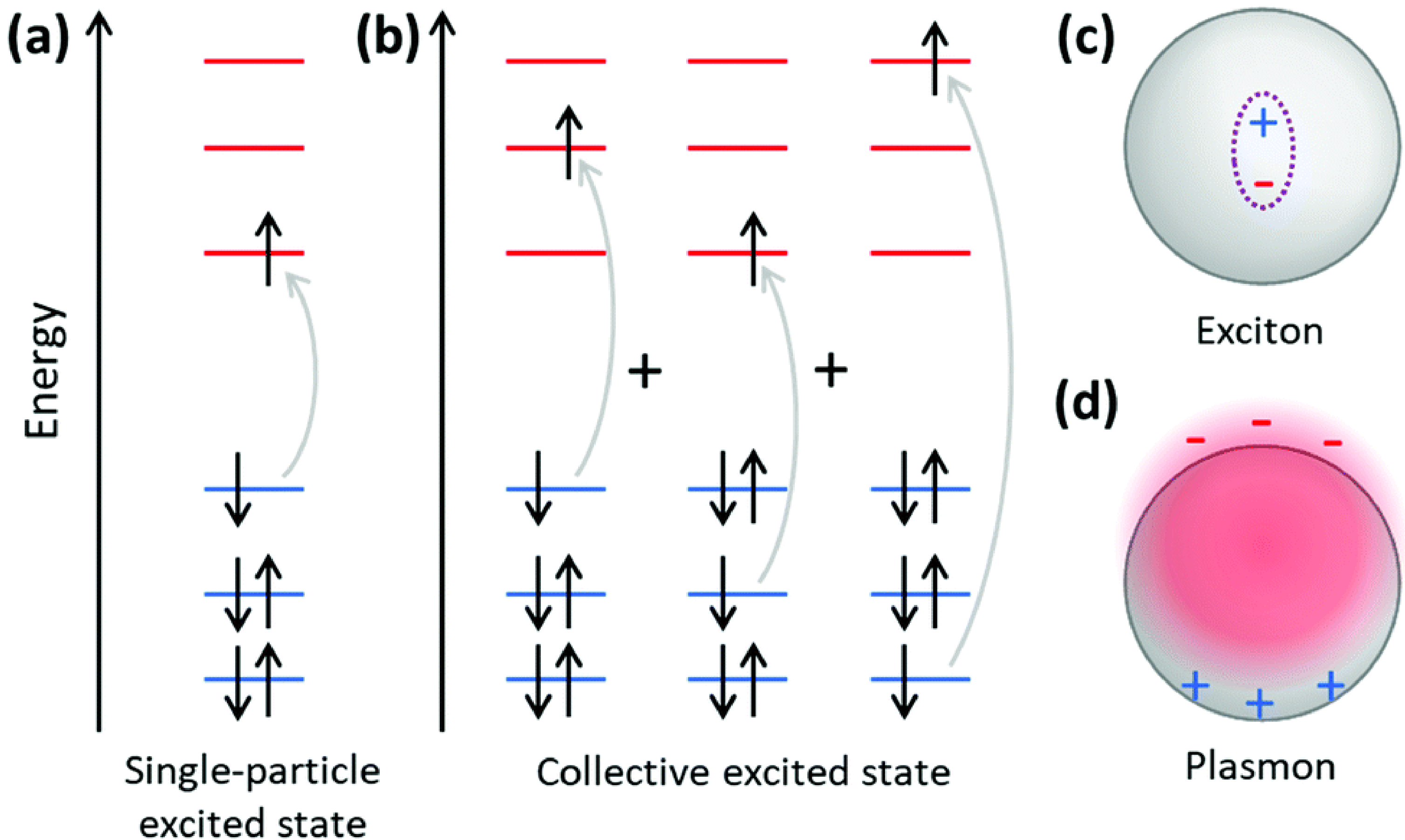
(a)
Energy
Single-particle
excited state
(b)
+
+
Collective excited state
(c)
Exciton
(d)
Plasmon

Motivation

- While this plasmon-to-exciton transition has been clear in spherical particles, it remains unclear in non-spherical (or anisotropic) cases such as rods
- In early theory, plasmon-like features in Au and Ag quantum rods (QRs) were predicted but there has been no experimental success yet
- They have experimentally attained a periodic series of gold QRs (Au_{42} to Au_{114} protected by the same thiolate), which exhibit unusual optical properties and shed light on the theoretical prediction more than a decade ago

Background Work

Materials Horizons

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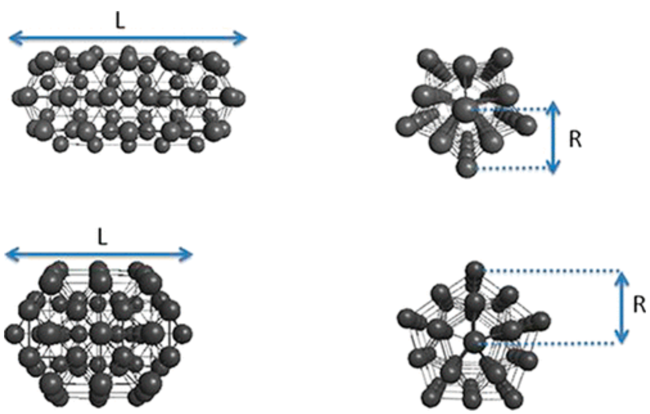
Plasmons: untangling the classical, experimental, and quantum mechanical definitions

Rebecca L. M. Gieseking



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Article

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Diameter Dependence of the Excitation Spectra of Silver and Gold Nanorods

Emilie B. Guidez and Christine M. Aikens*

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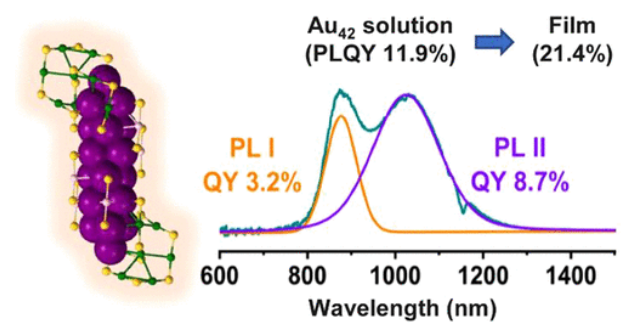
Communication

Near-Infrared Dual Emission from the $Au_{42}(SR)_{32}$ Nanocluster and Tailoring of Intersystem Crossing

Lianshun Luo,[#] Zhongyu Liu,[#] Xiangsha Du, and Rongchao Jin*



Introduction

- A periodic series of atomically precise gold quantum rods is reported Au_{42}, Au_{60}, Au_{78}, Au_{96}, Au_{114}
- These QRs possess hexagonal close-packed kernels with a constant three-atom diameter but increasing aspect ratios (ARs) from 6.3 to 18.7
- The kernels of the QRs are in a Au_1–$(Au_3)_n$–Au_1 configuration (where *n* is the number of Au_3 layers) and follow a periodic elongation with a uniform $Au_{18}(SR)_{12}$ increment consisting of four Au_3 layers
- These Au QRs possess distinct HOMO–LUMO gaps (Eg = 0.6 to 1.3 eV) and exhibit strongly polarized excitonic transition along the longitudinal direction, resulting in very intense absorption in the near-infrared (800 to 1,700 nm)

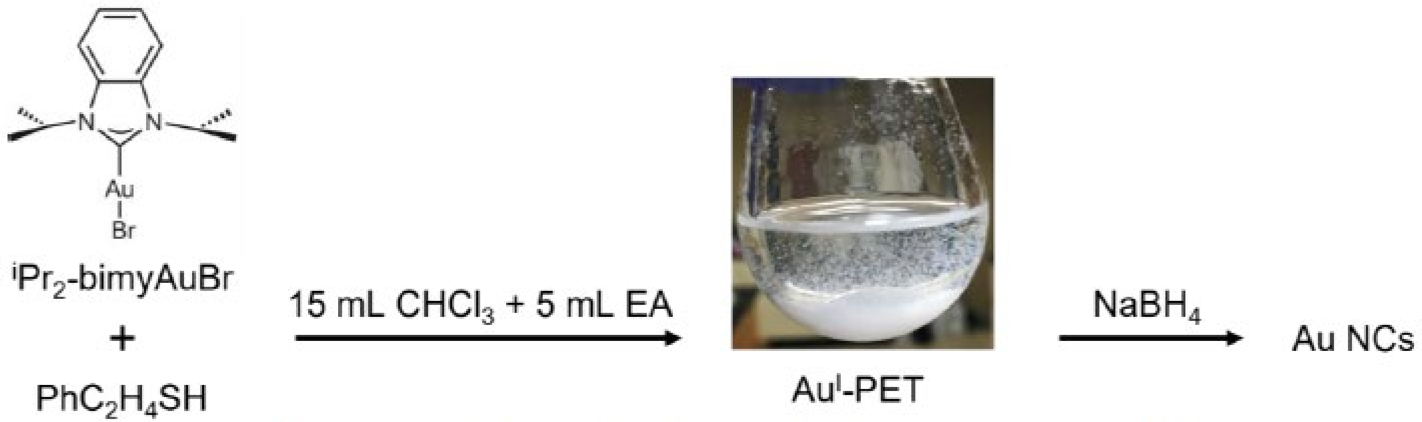
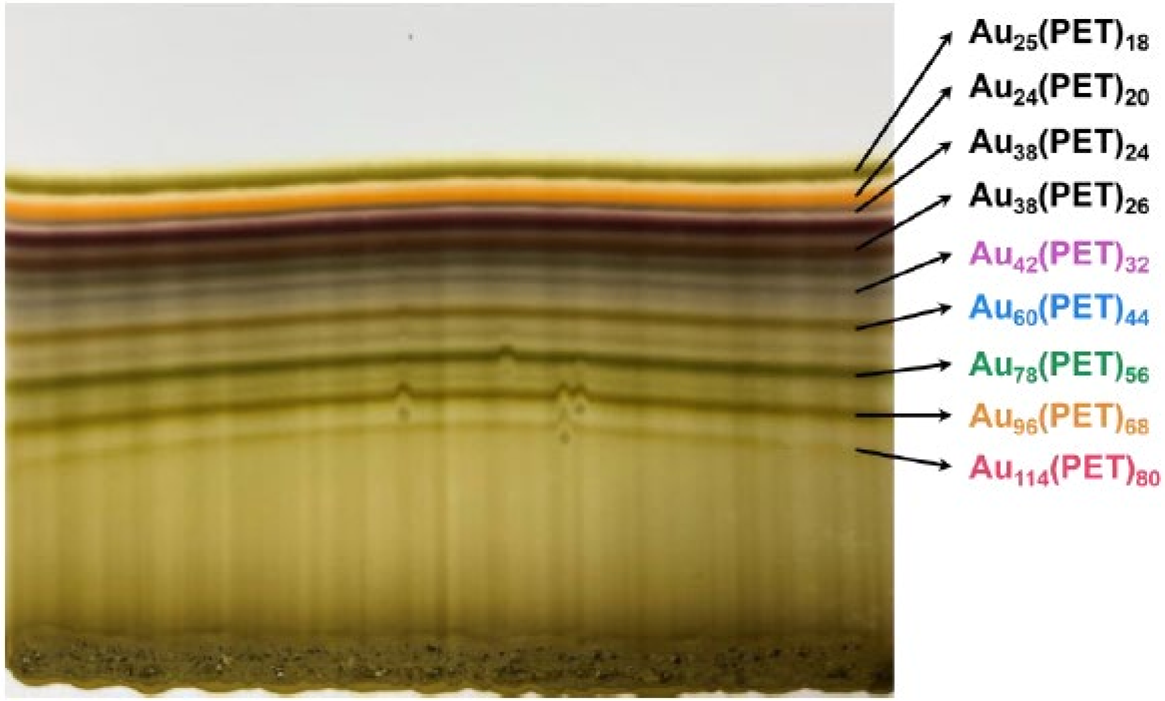
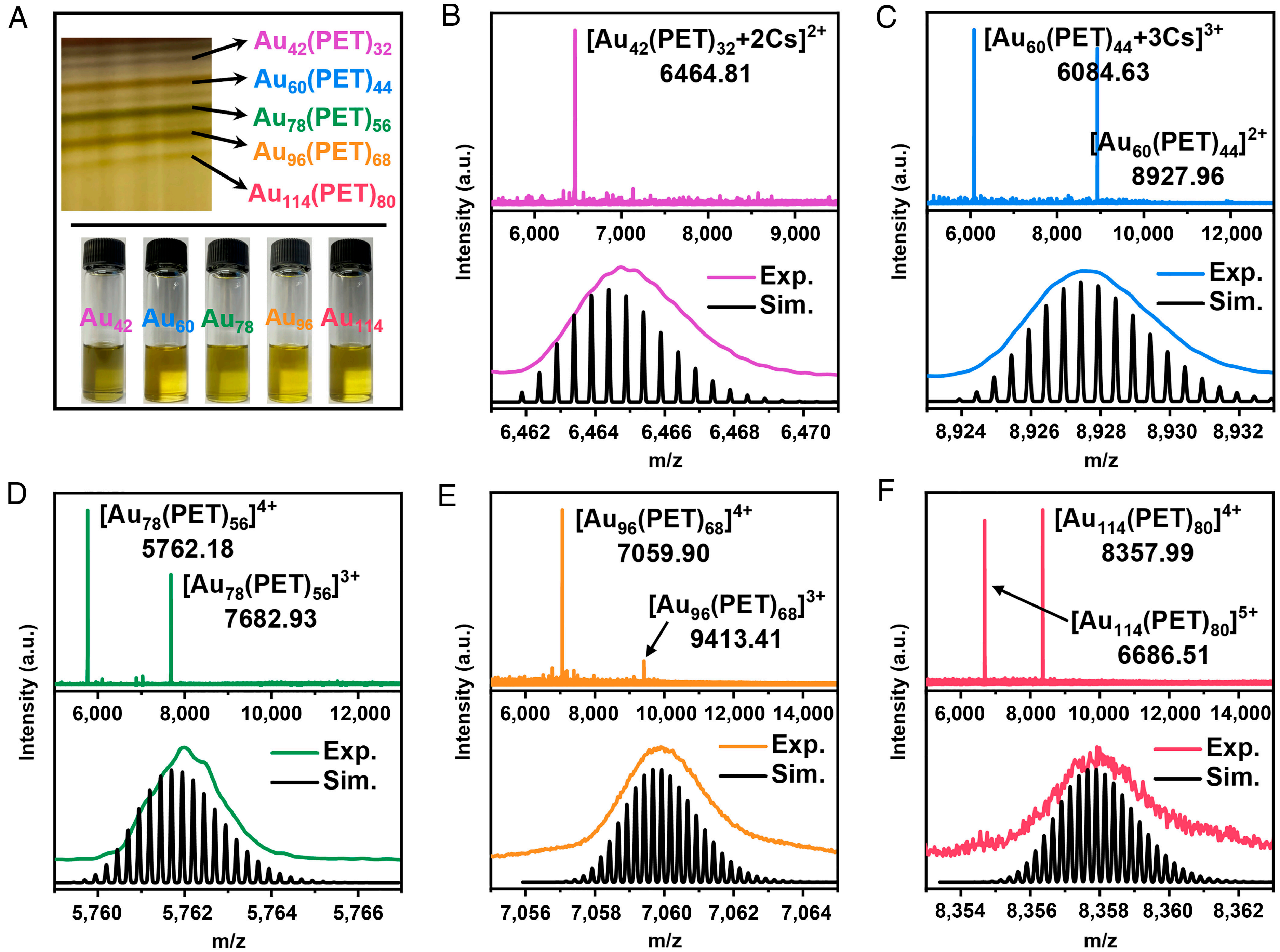


Figure S1. Illustration of the synthesis procedure for Au quantum rods (Au QRs).





A
Au42(PET)32
Au60(PET)44
Au78(PET)56
Au96(PET)68
Au114(PET)80
Au42 Au60 Au78 Au96 Au114
B
[Au42(PET)32+2Cs]2+
6464.81
Exp.
Sim.
Intensity (a.u.)
m/z
C
[Au60(PET)44+3Cs]3+
6084.63
[Au60(PET)44]2+
8927.96
Exp.
Sim.
Intensity (a.u.)
m/z
D
[Au78(PET)56]4+
5762.18
[Au78(PET)56]3+
7682.93
Exp.
Sim.
Intensity (a.u.)
m/z
E
[Au96(PET)68]4+
7059.90
[Au96(PET)68]3+
9413.41
Exp.
Sim.
Intensity (a.u.)
m/z
F
[Au114(PET)80]4+
8357.99
[Au114(PET)80]5+
6686.51
Exp.
Sim.
Intensity (a.u.)
m/z

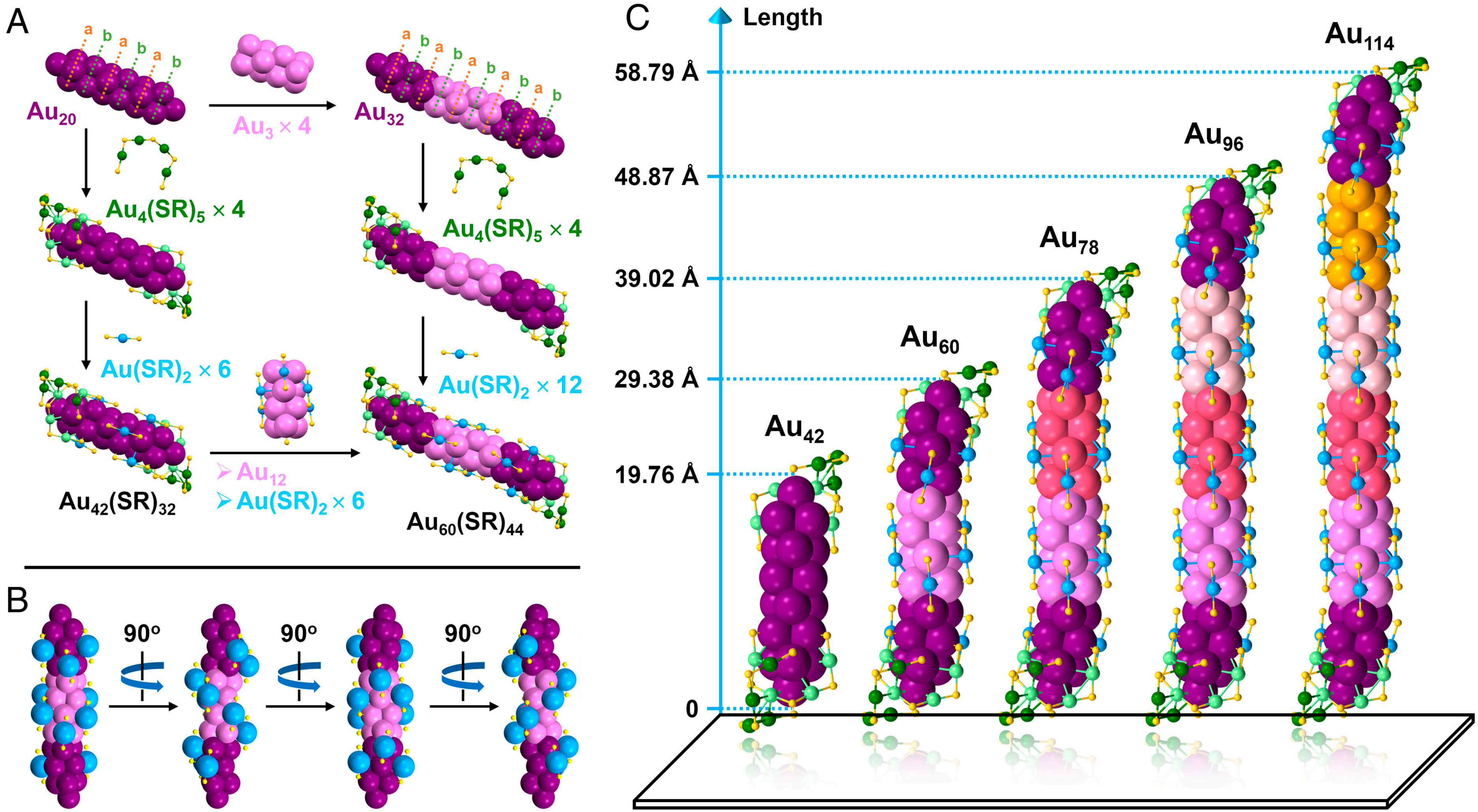


Fig. 2. (*A*) Illustration of the structural evolution from Au_{42} to Au_{60}. (*B*) Twelve $Au(PET)_2$ motifs wrapping the Au_{32} kernel of Au_{60} along the *C*3 axis. (*C*) Structure schematic of Au_{42}, Au_{60}, Au_{78}, Au_{96}, and Au_{114} with kernel length ranging from 19.76 to 58.79 Å. Color code: yellow = S, other colors = Au, carbon tails are omitted for clarity.

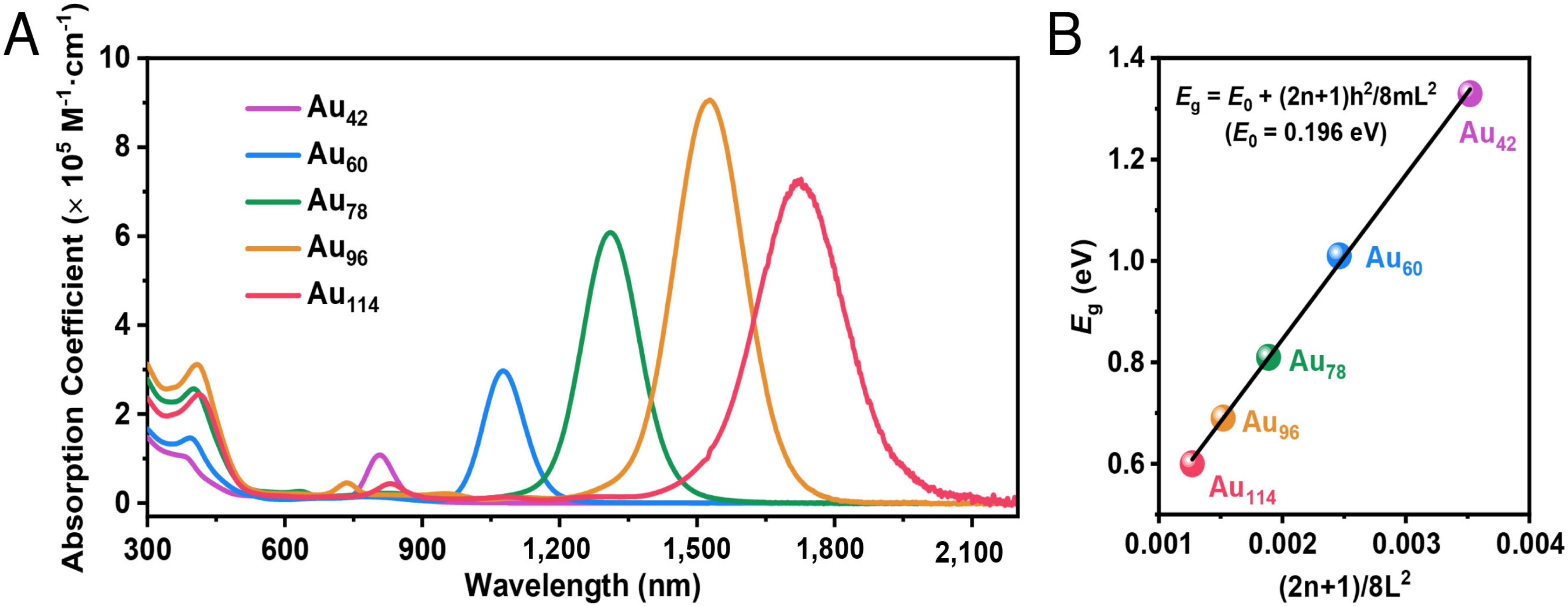
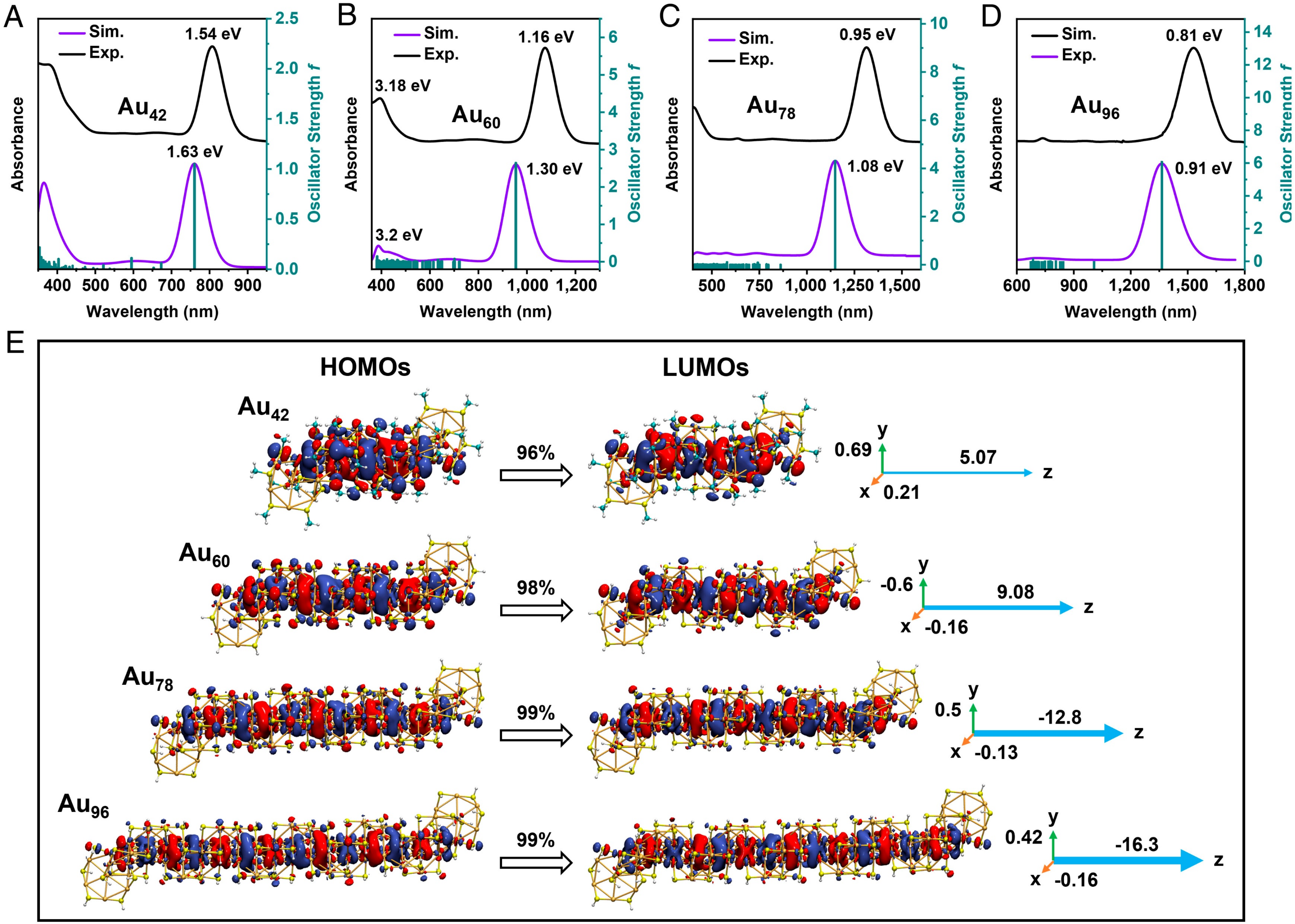


Fig. 3. (*A*) Optical absorption spectra of Au QRs. (*B*) Fitting of optical gaps by the Schrödinger equation for the 1D particle in a box; *L*: the length of Au QRs, *n*: the energy level, *m*: electron mass.


A
Sim.
Exp.
1.54 eV
Au42
1.63 eV
Absorbance
Oscillator Strength f
Wavelength (nm)
B
Sim.
Exp.
1.16 eV
3.18 eV
Au60
1.30 eV
3.2 eV
C
Sim.
Exp.
0.95 eV
Au78
1.08 eV
D
Sim.
Exp.
0.81 eV
Au96
0.91 eV
E
HOMOs
LUMOs
Au42
96%
0.69
5.07
0.21
Au60
98%
-0.6
9.08
-0.16
Au78
99%
0.5
-12.8
-0.13
Au96
99%
0.42
-16.3
-0.16

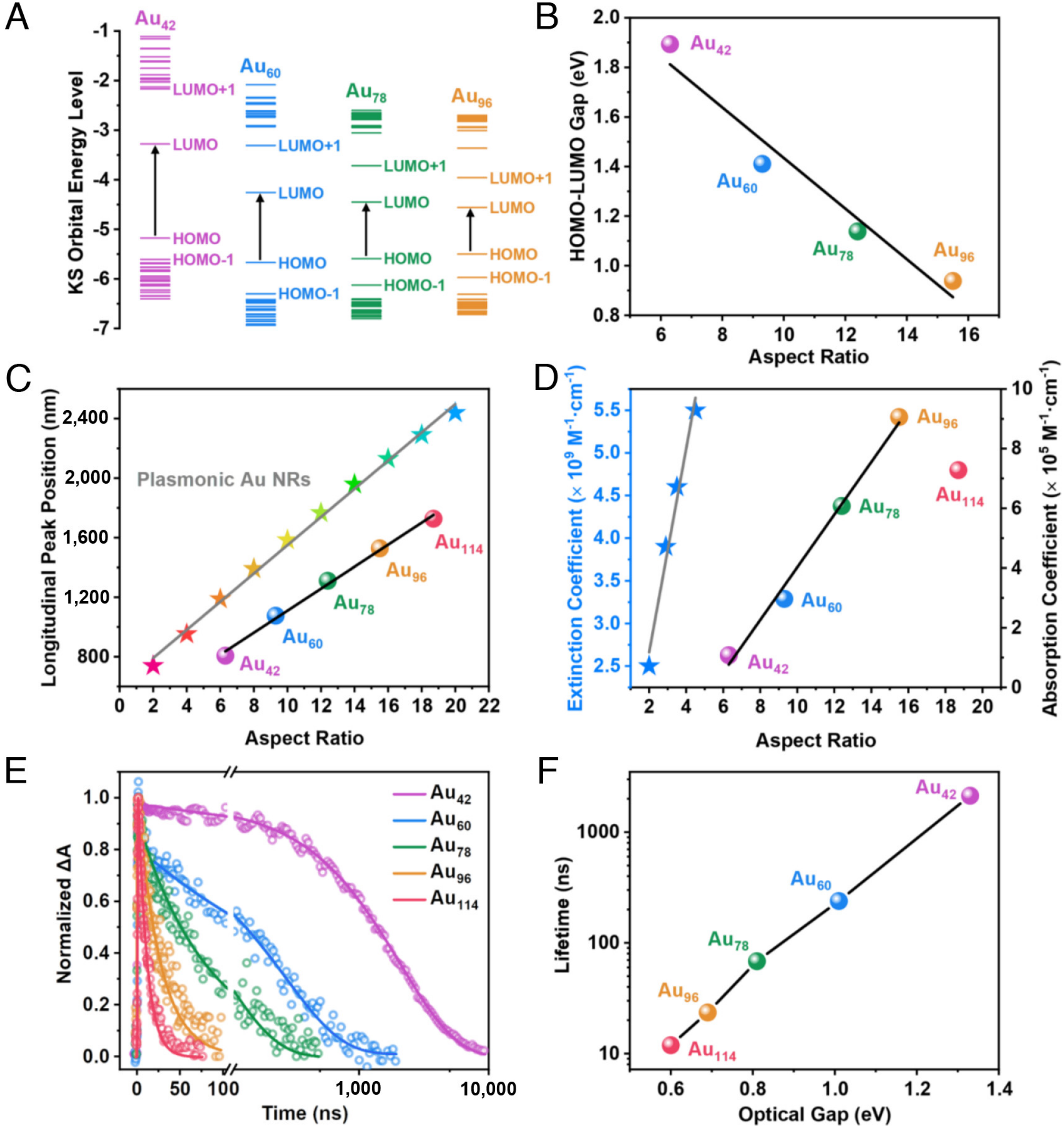


Fig. 5. (*A*) Kohn–Sham orbital energy level diagrams of Au_{42}, Au_{60}, Au_{78}, Au_{96}, and Au_{114}. (*B*) The HOMO–LUMO gap vs. the AR. (*C*) Variation of longitudinal extinction peak for simulated Au nanorods (diameter =10 nm, ARs from 2 to 20) (28) and ultrasmall Au QRs as the AR increases. (*D*) Variation of extinction coefficient for Au nanorods and ultrasmall Au QRs as the AR increases. (*E*) The ns-TA kinetics at 400 nm excitation and corresponding fits of Au_{42}, Au_{60}, Au_{78}, Au_{96}, and Au_{114}. (*F*) The *E*g gap dependent excited state lifetimes of Au_{42}, Au_{60}, Au_{78}, Au_{96}, and Au_{114}.

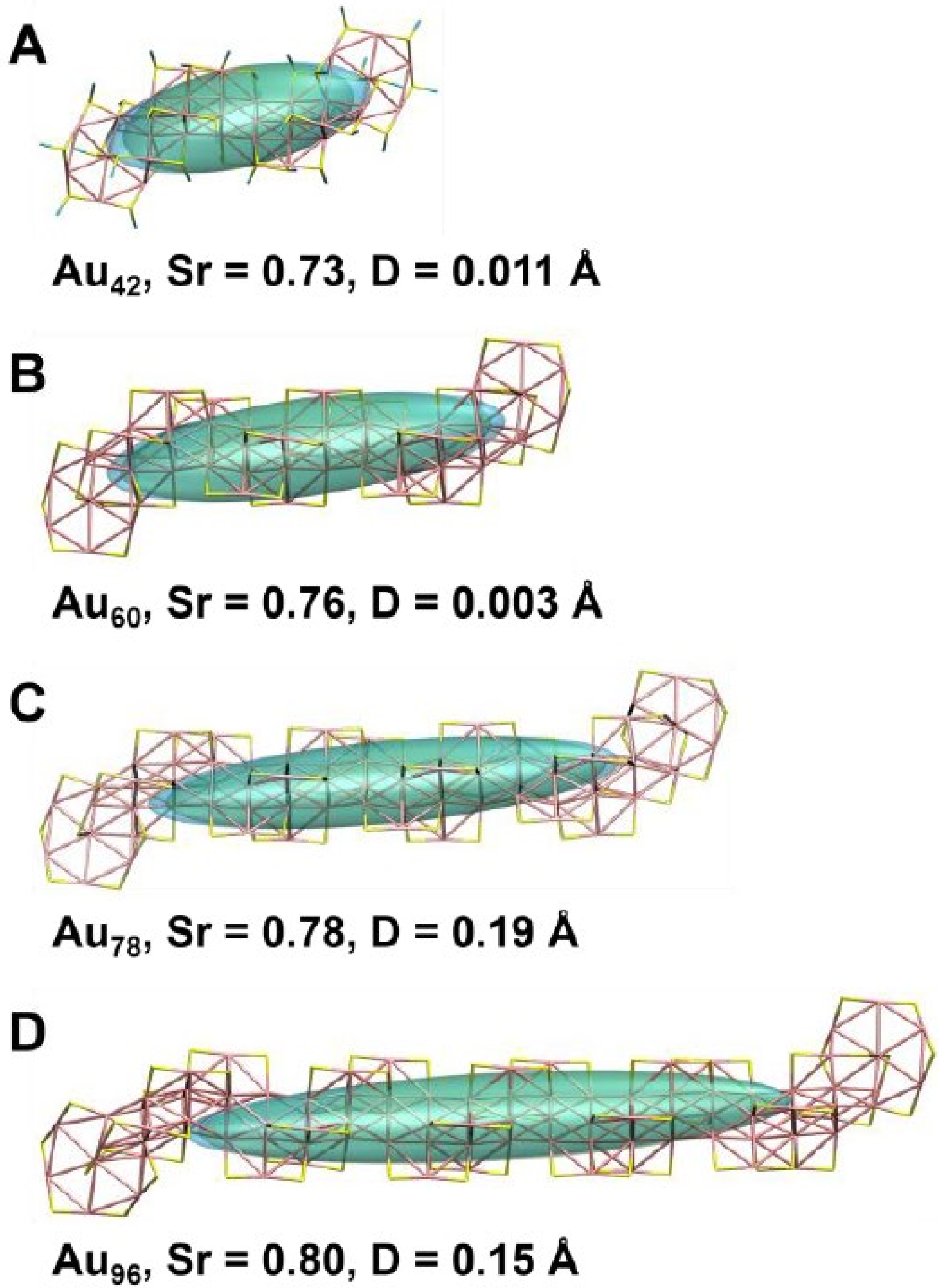


Figure S19. Distribution of the C_{hole} (color: lime) and $C_{electron}$ (color: cyan, largely overlapped) during the $S_0 \rightarrow S_1$ excitation in (A) Au_{42}, (B) Au_{60}, (C) Au_{78}, and (D) Au_{96} QRs. The C_{hole} and $C_{electron}$ diagram describes the overall trend distribution of hole and electron by Gaussian functions, erasing the distribution details.

- Strong transition dipole moment is a prerequisite to display plasmonic behavior
- Oscillator strength increases with AR

Plasmonic behaviour	Excitonic behaviour
➢ With higher AR, oscillator strength increases	➢ Larger HOMO-LUMO gap, 0.6 – 1.33 eV
➢ Linear relation of AR with extinction coefficient	➢ Higher exciton lifetime, 10 - 2122 ns
➢ Higher order of NIR extinction coefficient	➢ Fluence independent electron dynamics

Conclusion

- This work reports a periodic series of atomically precise gold quantum rods with unusual excitonic properties
- This work demonstrates that single-electron transition in Au QRs (Eg = 0.6 to 1.33 eV) may exhibit plasmon-like behavior, manifested by the strongly polarized longitudinal component due to the rod shape, the intense NIR peak, and its linear scaling relations with the AR
- Their excited states exhibit long lifetimes (10 to 2,122 ns), significantly longer than that of the classical plasmons (i.e., hundreds of femtoseconds)
- The long lifetimes of carriers renders the QRs quite promising in applications, such as solar cells and NIR photocatalysis