SUPPLEMENTARY MATERIAL

**Diarsine- vs Diphosphine-Protected Au13 Clusters: Effect of Subtle Geometric Differences on Optical Property and Electronic Structure**

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**I. Experimental Results**

**A. ORTEP Drawing**

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**Figure S1.** ORTEP drawing for **3**·(SbF6)3. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms are omitted.

**B. Crystal Data**

**Table S1.** Crystal data for **3**·(SbF6)3·5(C7H8)·CH2Cl2.

Empirical formula C171H172As10Au13Cl4F18Sb3

Formula weight 6385.89 g/mol

Temperature 98 K

Wavelength 1.54184 Å

Crystal size 0.082 × 0.053 × 0.019 mm3

Crystal system Monoclinic

Space group *C*2/c

Unit cell dimensions *a* = 31.5214(3) Å *α* = 90°

*b* = 22.12251(16) Å *β* = 90.0397(10)°

*c* = 51.6225(5) Å *γ* = 90°

Volume 35998.0(5) Å3

*Z* 8

Density (calculated) 2.357 Mg/m3

Absorption coefficient 25.991 mm-1

*F*(000) 23504

Theta range for data collection 2.440 to 51.645°

Index ranges −18 ≤ h ≤ 32, −22 ≤ k ≤ 20, −52 ≤ l ≤ 45

Reflections collected 36069

Independent reflections 16676 [*R*(int) = 0.0271]

Completeness to theta = 50.38° 85.34 %

Absorption correction Multi-scan

Max. and min. transmission 1.00000 and 0.27419

Refinement method Full-matrix least-squares on *F*2

Data / restraints / parameters 16676 / 408 / 1826

Goodness-of-fit on *F*2 1.085

Reflections with *I* > 2**(*I*) 14017

Final *R* indices [*I* > 2**(*I*)] *R1* = 0.0457, *wR*2 = 0.1236

*R* indices (all data) *R1* = 0.0556, *wR*2 = 0.1291

Largest diff. peak and hole +2.868 and −1.472 eÅ-3

**C. Angles and Distances of the Pentagonal Antiprismatic Unit**

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**Figure S2.** Angles (*θ*1 and *θ*2) and distances (d1 and d2) of the pentagonal antiprismatic unit of **3**. Areas relating to cross-linked diarsines are shaded in aqua.

**D. Absorption and photoluminescence spectra**

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**Figure S3.** Absorption (blue line) and photoluminescence (red line; *λ*ex = 450 nm) spectra of **2**·Cl3 in MeCN.

**II. Computational Results**

**A. Geometry Optimization**

**Table S2.** Average distances (d1, d2, d3, z1 and r1) and angles (*θ*1 − 36 and *θ*2 − 36) of the geometry-optimized Au13 clusters (with standard deviations) *a*

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | d1 (Å) | d2 (Å) | d3 (Å) | z1 (Å) | r1 (Å) | *θ*1 – 36 (º) | *θ*2 – 36 (º) |
|  | **1** | 2.962 ± 0.001 | 3.046 ± 0.002 | 3.046 ± 0.002 | 5.559 | 2.885 ± 0.000 | −1.66 ± 0.07 | +1.66 ± 0.06 |
|  |  | [2.961, 2.963] | [3.043, 3.048] | [3.043, 3.048] |  | [2.884, 2.885] | [−1.79, −1.62] | [+1.55, +1.72] |
|  | **3** | 3.042 ± 0.007 | 3.039 ± 0.033 | 3.039 ± 0.033 | 5.591 | 2.889 ± 0.016 | +0.25 ± 0.45 | −0.25 ± 0.98 |
|  |  | [3.036, 3.054] | [2.985, 3.089] | [2.985, 3.089] |  | [2.863, 2.915] | [−0.41, +0.93] | [−1.57, +1.27] |

*a* The minimum and maximum values are given in square brackets.

**B. Molecular Orbitals**

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**Figure S4.** Selected molecular orbitals of **1**. Their assignments as the superatomic P and D orbitals are indicated on the right.

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**Figure S5.** Selected molecular orbitals of **3**. Their assignments as the superatomic P and D orbitals are indicated on the right.

**C. Molecular-Orbital and Electron-Transition Data**

**Table S3.** Kohn-Sham orbitals, energies, and atomic orbital contributions of **1**.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | MO | Orbital  index | Orbital energy (eV) /  Relative energy (eV) | % Au (*sp*) | % Au (*d*) | % P (*p*) | % Cl (*p*) |
|  | LUMO+4 | 669a | -7.00 / 3.11 | 61 | 19 | 6 | 12 |
|  | LUMO+3 | 668a | -7.16 / 2.95 | 70 | 3 | 13 | 0 |
|  | LUMO+2 | 667a | -7.16 / 2.95 | 70 | 3 | 13 | 0 |
|  | LUMO+1 | 666a | -7.29 / 2.82 | 70 | 0 | 13 | 1 |
|  | LUMO | 665a | -7.29 / 2.82 | 70 | 0 | 13 | 1 |
|  |  |  |  |  |  |  |  |
|  | HOMO | 664a | -10.11 / 0.00 | 46 | 14 | 19 | 4 |
|  | HOMO-1 | 663a | -10.11 / 0.00 | 45 | 14 | 19 | 4 |
|  | HOMO-2 | 662a | -10.77 / -0.67 | 42 | 16 | 8 | 22 |

**Table S4.** Kohn-Sham orbitals, energies, and atomic orbital contributions of **3**.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | MO | Orbital  index | Orbital energy (eV) /  Relative energy (eV) | % Au (*sp*) | % Au (*d*) | % As (*p*) | % Cl (*p*) |
|  | LUMO+4 | 779a | -7.19 / 3.10 | 66 | 9 | 9 | 5 |
|  | LUMO+3 | 778a | -7.23 / 3.07 | 69 | 3 | 11 | 1 |
|  | LUMO+2 | 777a | -7.25 / 3.04 | 65 | 11 | 8 | 7 |
|  | LUMO+1 | 776a | -7.36 / 2.94 | 66 | 5 | 12 | 0 |
|  | LUMO | 775a | -7.40 / 2.89 | 66 | 5 | 11 | 0 |
|  |  |  |  |  |  |  |  |
|  | HOMO | 774a | -10.29 / 0.00 | 43 | 13 | 18 | 4 |
|  | HOMO-1 | 773a | -10.30 / -0.01 | 42 | 14 | 18 | 4 |
|  | HOMO-2 | 772a | -10.63 / -0.33 | 41 | 16 | 13 | 13 |

**Table S5.** Excited states, energies, oscillator strengths and primary orbital-orbital transitions of **1**. H-*X* and L+*Y* in the nature of transition represent HOMO-*X* and LUMO+*Y*, respectively.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Excitation  index | Energy (eV) /  Wavelength (nm) | Oscillator strength | Dominant transition | Nature of transition |
|  | 1 | 2.15 / 577 | 5.24 × 10-8 | 664a→665a, 663a→666a | H→L, H-1→L+1 |
|  | 2 | 2.17 / 571 | 1.45 × 10-6 | 663a→666a, 664a→665a,  663a→665a, 664a→666a | H-1→L+1, H→L,  H-1→L, H→L+1 |
|  | 3 | 2.17 / 571 | 3.38 × 10-7 | 664a→666a, 663a→665a,  663a→666a, 664a→665a | H→L+1, H-1→L, H-1→L+1, H→L |
|  | 4 | 2.31 / 536 | 5.55 × 10-5 | 664a→667a, 663a→668a,  663a→667a, 664a→668a | H→L+2, H-1→L+3, H-1→L+2, H→L+3 |
|  | 5 | 2.31 / 536 | 2.36 × 10-5 | 663a→667a, 664a→668a,  664a→667a, 663a→668a | H-1→L+2, H→L+3, H→L+2, H-1→L+3 |
|  | 6 | 2.34 / 529 | 1.01 × 10-1 | 663a→665a, 664a→666a,  663a→666a, 664a→665a | H-1→L, H→L+1, H-1→L+1, H→L |
|  | 7 | 2.36 / 525 | 2.53 × 10-2 | 663a→669a, 664a→668a,  663a→667a | H-1→L+4, H→L+3, H-1→L+2 |
|  | 8 | 2.36 / 525 | 2.52 × 10-2 | 664a→669a, 663a→668a,  664a→667a | H→L+4, H-1→L+3, H→L+2 |
|  | 9 | 2.48 / 501 | 8.38 × 10-2 | 664a→669a, 663a→668a,  664a→667a | H→L+4, H-1→L+3, H→L+2 |
|  | 10 | 2.48 / 501 | 8.33 × 10-2 | 663a→669a, 664a→668a,  663a→667a | H-1→L+4, H→L+3, H-1→L+2 |
|  | 11 | 2.88 / 431 | 8.13 × 10-2 | 662a→665a | H-2→L |
|  | 12 | 2.88 / 431 | 8.09 × 10-2 | 662a→666a | H-2→L+1 |
|  | 13 | 2.96 / 419 | 5.35 × 10-6 | 662a→667a | H-2→L+2 |
|  | 14 | 2.96 / 419 | 5.72 × 10-7 | 662a→668a | H-2→L+3 |

**Table S6.** Excited states, energies, oscillator strengths and primary orbital-orbital transitions of **3**. H-*X* and L+*Y* in the nature of transition represent HOMO-*X* and LUMO+*Y*, respectively.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Excitation  index | Energy (eV) /  Wavelength (nm) | Oscillator strength | Dominant transition | Nature of transition |
|  | 1 | 2.28 / 544 | 5.28 × 10-3 | 773a→775a, 774a→775a | H-1→L, H→L |
|  | 2 | 2.28 / 543 | 3.13 × 10-3 | 774a→775a, 773a→776a,  773a→775a | H→L, H-1→L+1,  H-1→L |
|  | 3 | 2.33 / 532 | 1.66 × 10-2 | 774a→776a, 773a→777a,  774a→777a | H→L+1, H-1→L+2,  H→L+2 |
|  | 4 | 2.36 / 526 | 1.04 × 10-2 | 774a→777a, 773a→777a,  773a→776a | H→L+2, H-1→L+2,  H-1→L+1 |
|  | 5 | 2.41 / 515 | 2.46 × 10-2 | 774a→778a, 773a→777a | H→L+3, H-1→L+2 |
|  | 6 | 2.43 / 510 | 2.48 × 10-2 | 774a→778a, 773a→777a | H→L+3, H-1→L+2 |
|  | 7 | 2.45 / 506 | 4.57 × 10-3 | 774a→779a, 773a→778a | H→L+4, H-1→L+3 |
|  | 8 | 2.46 / 503 | 7.32 × 10-2 | 774a→777a, 773a→776a | H→L+2, H-1→L+1 |
|  | 9 | 2.49 / 498 | 5.93 × 10-2 | 773a→779a | H-1→L+4 |
|  | 10 | 2.57 / 482 | 8.38 × 10-2 | 774a→779a, 773a→778a,  772a→775a | H→L+4, H-1→L+3,  H-2→L |
|  | 11 | 2.59 / 479 | 1.98 × 10-2 | 772a→775a | H-2→L |
|  | 12 | 2.63 / 471 | 5.45 × 10-3 | 772a→776a | H-2→L+1 |
|  | 13 | 2.84 / 437 | 1.32 × 10-1 | 772a→777a | H-2→L+2 |
|  | 14 | 2.85 / 435 | 1.65 × 10-1 | 772a→778a | H-2→L+3 |
|  | 15 | 2.89 / 430 | 7.10 × 10-2 | 772a→779a | H-2→L+4 |