Electronic Supplementary Material (ESI) for Nanoscale Advances.

Electronic Supplementary Information

Electron Transport Properties of PAl_{12}-Based Cluster Complexes

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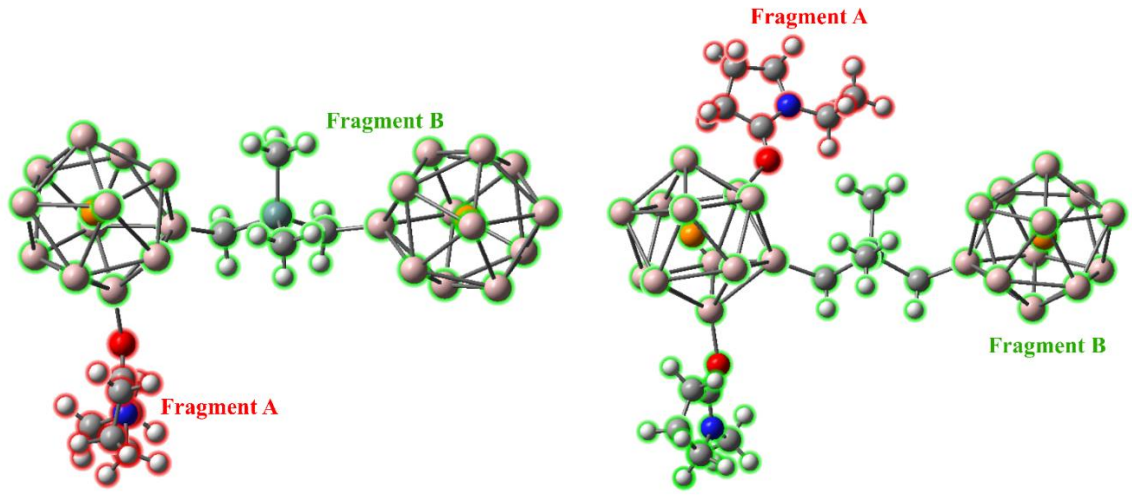


(a) **(b)**

Figure S1. Test calculations of basis set superposition error (BSSE) for (a) $(EP)_1PAl_{12}[Ge_B]PAl_{12}$ and (b) $(EP)_2PAl_{12}[Ge_B]PAl_{12}$.

Note: summary of BSSE results.

(a) Level of Theory: PBE/TZ2P+scalar-rel ZORA

BSSE (fragment A) = 0.0199 eV

BSSE (fragment B) = 0.0264 eV

Net Total BSSE for **$(EP)_1PAl_{12}Ge^2_BPAl_{12}$ = 0.0463 eV** (1.07 kcal/mol).

(b) Level of Theory: PBE/TZ2P+scalar-rel ZORA

BSSE (fragment A) = 0.0228 eV

BSSE (fragment B) = 0.0265 eV

Net Total BSSE for **$(EP)_2PAl_{12}Ge^2_BPAl_{12}$ = 0.0493 eV** (1.13 kcal/mol).

(a) (b)

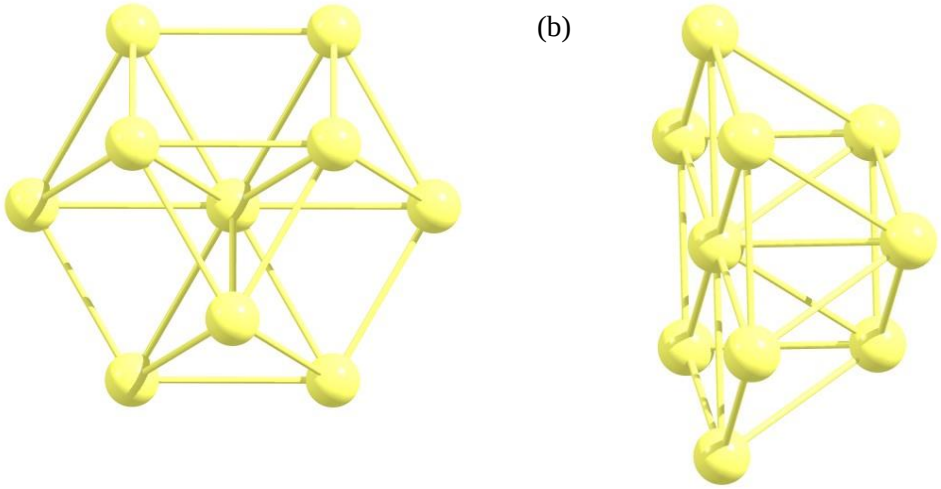
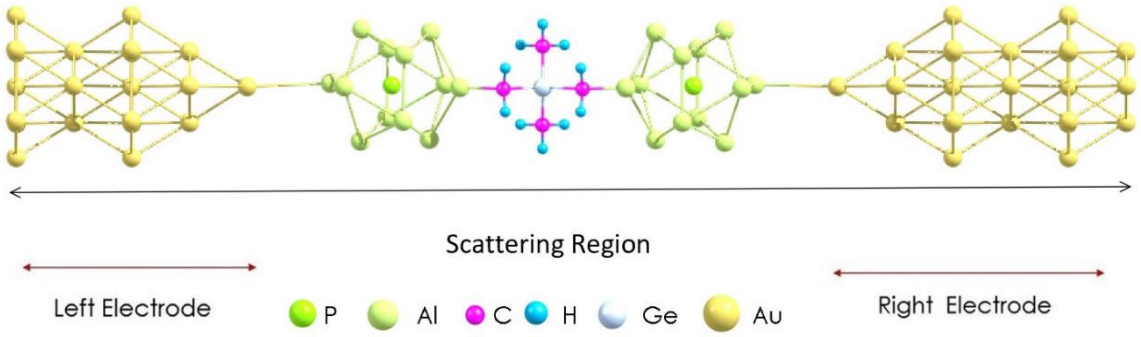
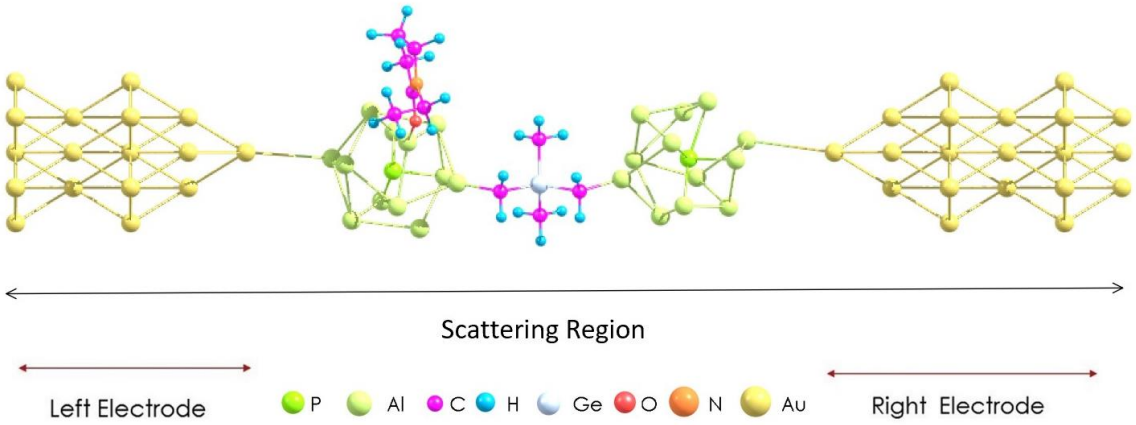


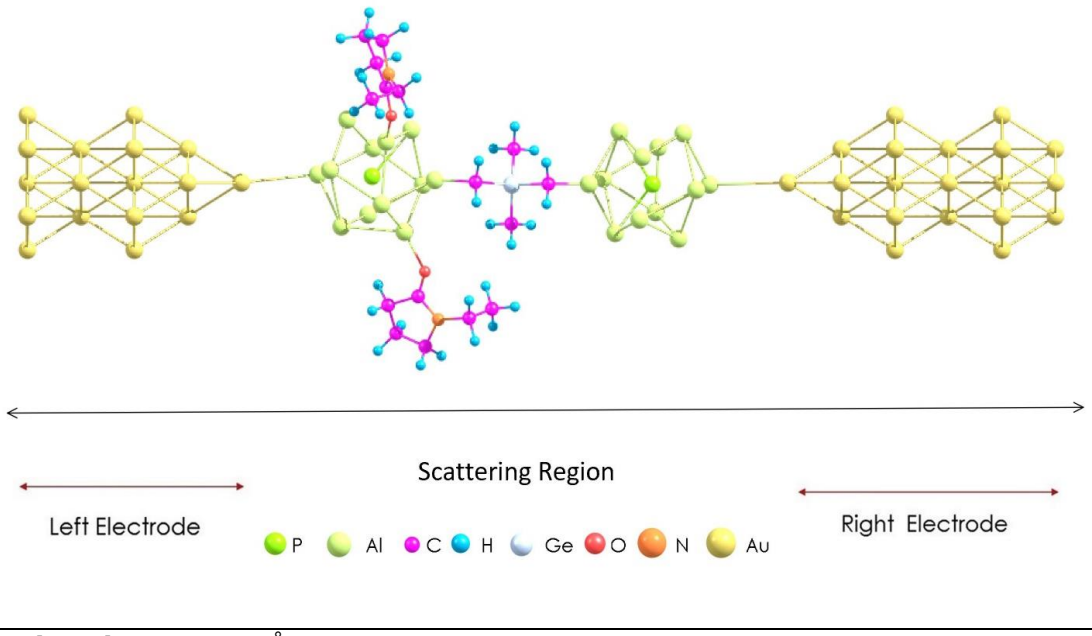
Figure S2. Structure model for the Au electrode in (a) top view, and (b) side view.



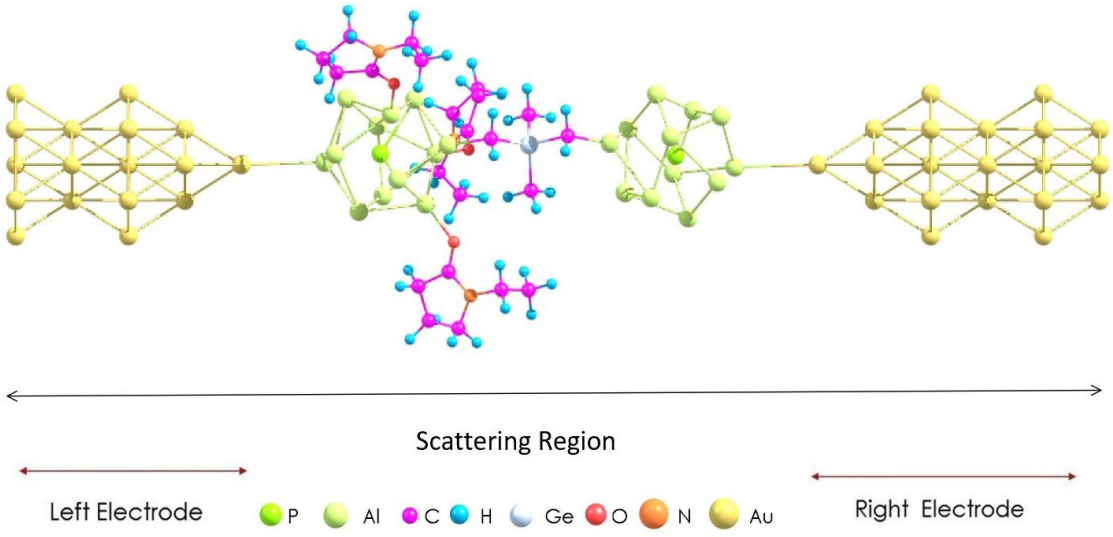
EP0: Al-Au distance: 3.50 Å



EP1: Al-Au distance: 3.92 Å



EP2: Al-Au distance: 3.62 Å



EP3: Al-Au distance: 3.54 Å

Figure S3. The device configuration consisting of the Au electrode and $(EP)_nPAl_{12}[Ge_B]PAl_{12}$ (n = 0-3) cluster complex with zero, one, two, and three ligands (labeled as EP0, EP1, EP2, and EP3). The shortest distance between Al and Au is also labeled.

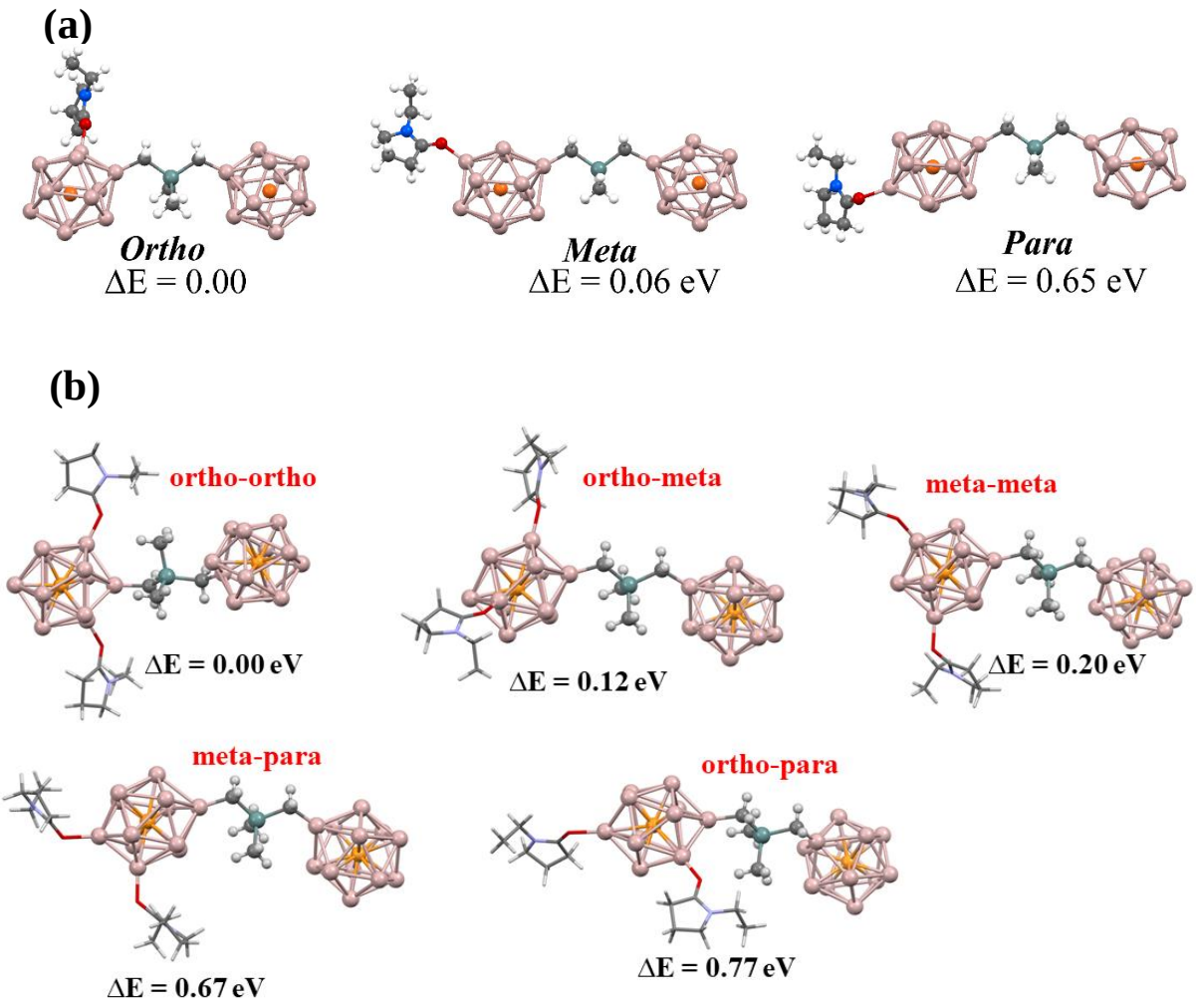


Figure S4. Various conformers of (a) $(EP)_1PAl_{12}[Ge_B]PAl_{12}$ and (b) $(EP)_2PAl_{12}[Ge_B]PAl_{12}$. Relative energies ΔE (in eV) are listed for all configurations. The lowest energy configurations are chosen and used for electron transport calculations.

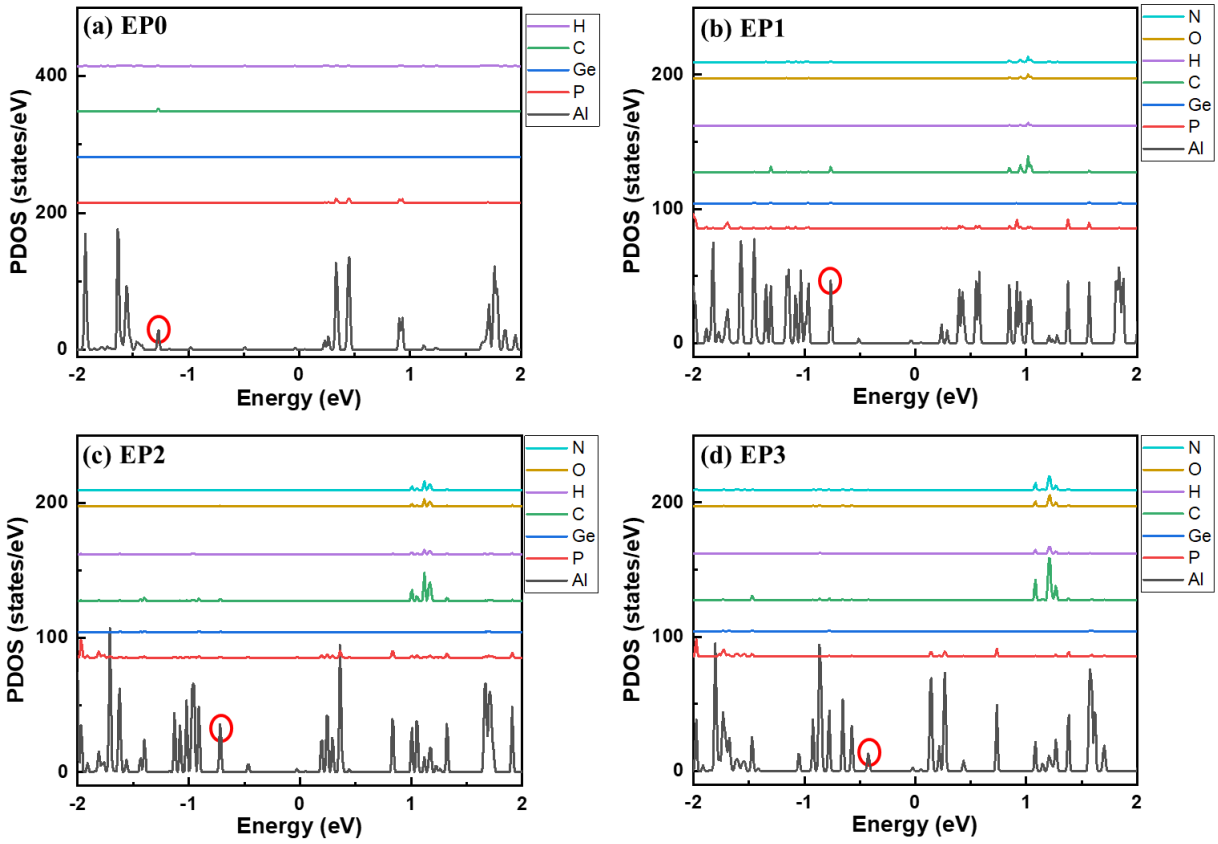


Figure S5. Projected density of states (PDOS) of the $(EP)_nPAl_{12}[Ge_B]PAl_{12}$ (n = 0-3) cluster complexes in contact with Au electrodes with zero (EP0), one (EP1), two (EP2), and three (EP3) ligands. The zero of the energy is aligned to the Fermi energy. The peak corresponding to the first significant transmission orbital below the Fermi level is labeled by a red circle. The major contribution to these peaks is from the cluster atom, Al.

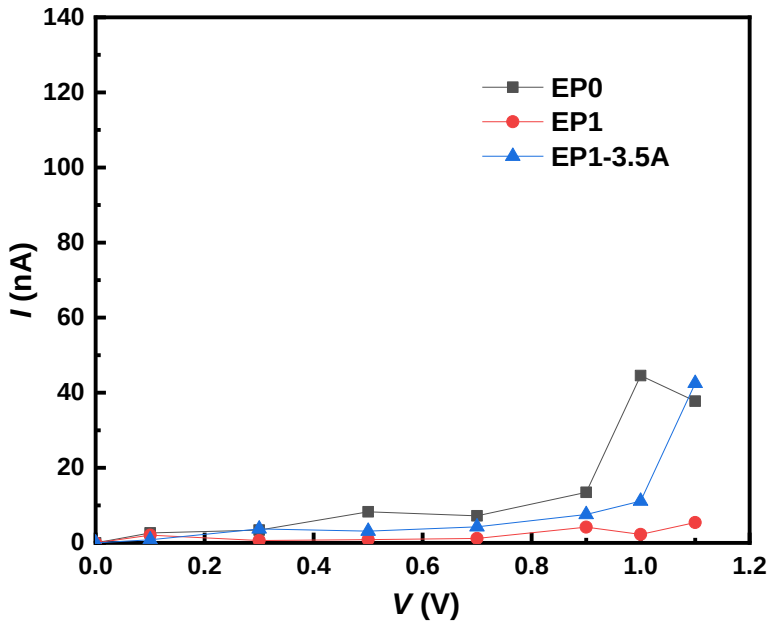
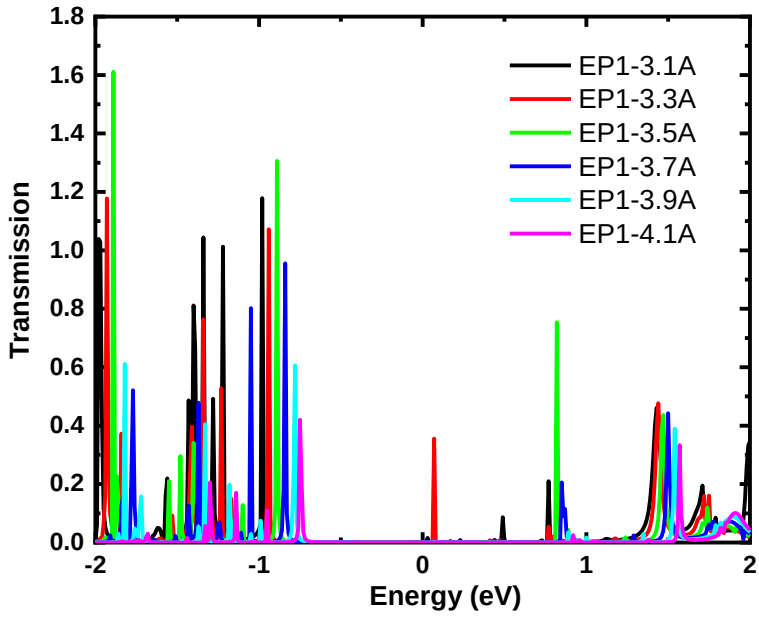
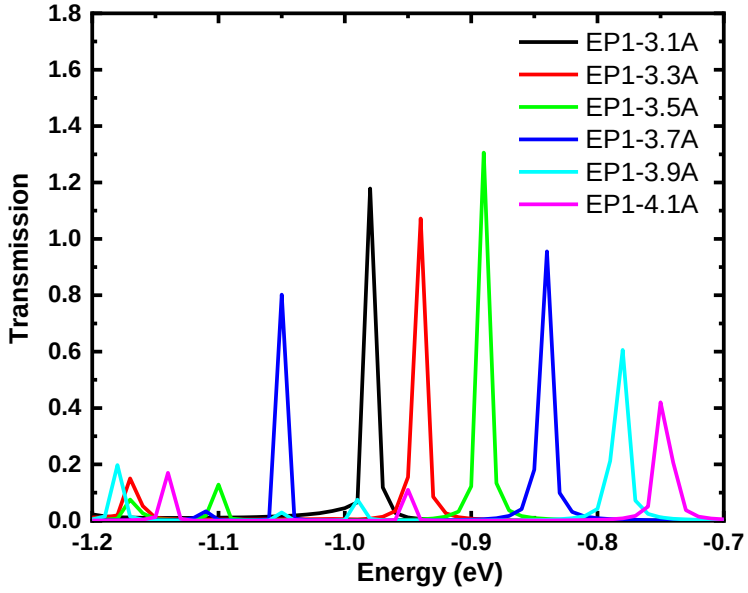


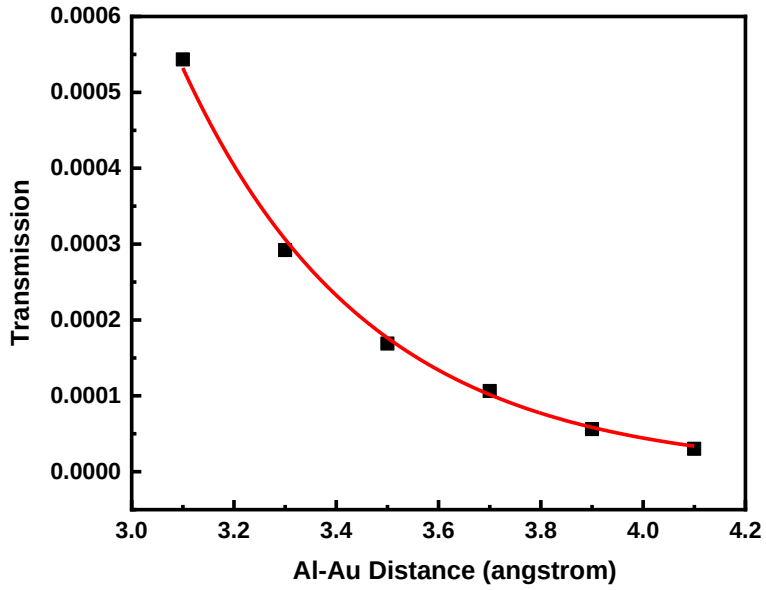
Figure S6. The current-voltage characteristics of the $(EP)_nPAl_{12}[Ge_B]PAl_{12}$ cluster complexes: EP0 with an Al-Au distance of 3.5 Å, EP1 with an Al-Au distance of 3.9 Å, and EP1-3.5A with an Al-Au distance of 3.5 Å.


Transmission
Energy (eV)
EP1-3.1A
EP1-3.3A
EP1-3.5A
EP1-3.7A
EP1-3.9A
EP1-4.1A
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-2
-1
0
1
2

(a)


Transmission
Energy (eV)
EP1-3.1A
EP1-3.3A
EP1-3.5A
EP1-3.7A
EP1-3.9A
EP1-4.1A
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7

(b)



(c)

Figure S7. Transmission functions of the $(EP)_1Al_{12}P[Ge_B]Al_{12}P$ cluster complex EP1 at 0 V for different Al (cluster)-Au (electrode) distances (a) within the energy range of -2.0 ~ 2.0 eV; (b) zoomed into the range of -1.2 ~ -0.7 eV to see the variation of the first significant transmission peak below the Fermi level. The zero of the energy is aligned to the Fermi energy. The transmission value at 0 eV is plotted as a function of the Al (cluster)-Au (electrode) distance in (c), which follows an exponential decay (the red line).

Table S1. Comparison of the calculated HOMO−LUMO gap of the three optimized cluster complexes (EP1, EP2, and EP3) from PBE and B3LYP functionals using the same basis set (TZ2P).

PBE (As reported in the paper)			
System	EP1	EP2	EP3
HOMO-LUMO Gap (eV)	1.14	0.60	0.21
HOMO (eV)	-4.18	-3.62	-3.26
LUMO (eV)	-3.04	-3.02	-3.05
B3LYP (20% HF exchange)			
System	EP1	EP2	EP3
HOMO-LUMO Gap (eV)	2.00	1.40	0.96
HOMO (eV)	-4.39	-3.77	-3.38
LUMO (eV)	-2.39	-2.37	-2.42

Note: As seen from the table, for all three systems, the B3LYP calculated HOMO−LUMO gaps are 0.75-0.86 eV higher than GGA-PBE. Although the magnitude of the gap has changed, the relative trend remained the same. As we proceed from EP1 to EP3, the HOMO−LUMO gap is gradually reducing, as reported in the paper. Furthermore, the energies of the HOMO and LUMO levels are also altering similarly.

Cartesian coordinates of optimized ground state structures of $(EP)_nPAl_{12}[Ge_B]PAl_{12}$ (n= 0-3)

$PAl_{12}[Ge_B]PAl_{12}$

41

XYZ

P -0.043747 0.292629 -6.228118
Al -2.201637 0.199426 -4.675824
Al -1.581587 2.377416 -6.342846
Al 0.065293 -1.01401 -3.476046
Al -1.231905 -2.048675 -5.789868
Al -0.122933 1.776992 -4.026275
Al -2.293853 -0.066465 -7.469431
Al 1.199779 2.560266 -6.370641
Al -0.148297 1.462896 -8.681599
Al 1.448348 -1.871577 -5.818045
Al 2.135598 0.486291 -4.717151
Al 0.0484 -1.38302 -8.204109
Al 2.204139 0.232578 -7.512329
Al -1.159481 -2.23582 5.672729
Al 1.518059 -2.031043 5.672877
Al 0.100445 -1.102459 3.379542
Al 0.142279 -1.642087 8.090886
Al -2.163178 0.040659 4.649532
Al 2.170462 0.370353 4.650553
P 0.010186 0.101407 6.178327
Al -2.219948 -0.322926 7.432874
Al 2.275007 0.016595 7.432374
Al -0.10827 1.664664 4.032379
Al -0.074207 1.182806 8.673498
Al -1.544797 2.164711 6.385833
Al 1.23538 2.374463 6.388298
H -2.517518 -0.427149 -0.034114
C -1.677058 0.277377 -0.021449
H -0.662609 -2.670613 1.504259
H -1.741922 0.89212 0.884915
H -1.744084 0.927205 -0.902755
H -0.653273 -2.63966 -1.631371
C 0.168118 -1.952085 1.593069
Ge 0.070661 -0.746282 -0.042486
C 0.164765 -1.905512 -1.711294
H 1.102972 -2.528913 1.505163
H 1.109065 -2.470431 -1.649614
C 1.629167 0.546922 -0.025941
H 1.596287 1.163959 0.880612
H 1.588455 1.198807 -0.907308
H 2.572789 -0.011979 -0.040915

$(EP)_1PAl_{12}[Ge_B]PAl_{12}$

60

XYZ

P 0.5245 1.538 -5.37507
Al -1.35569 1.15659 -3.54
Al -1.04413 3.53517 -5.03134
Al 1.02013 -0.08812 -2.80903
Al -0.67027 -1.01125 -4.96505
Al 0.76167 2.7451 -3.06002
Al -1.88926 1.17961 -6.24448
Al 1.7577 3.86859 -5.51717
Al 0.02624 2.84941 -7.64387
Al 1.9553 -0.70622 -5.34941
Al 2.86852 1.54936 -4.20737
Al 0.26952 -0.03943 -7.42243
Al 2.52697 1.52321 -6.97658
Al -0.61908 -2.4123 5.86302
Al 1.92793 -1.79931 6.44694
Al 0.8522 -0.85098 3.97406
Al 0.05502 -1.89895 8.54447
Al -1.78162 -0.22015 4.82853
Al 2.33447 0.7723 5.77436
P 0. 0. 6.78593
Al -2.32142 -0.89626 7.49955
Al 1.95464 0.13223 8.4827
Al 0.03718 1.75867 4.7897
Al -0.75948 0.77495 9.2815
Al -1.90033 1.76694 6.81351
Al 0.74495 2.39983 7.42336
H -1.49847 -0.2648 0.59047
C -0.78365 0.5638 0.67669
H 0.8126 -2.37033 1.9205
H -0.96325 1.08951 1.62212
H -0.94091 1.25672 -0.15923
H 0.75402 -2.01867 -1.11753
C 1.38247 -1.45997 2.16823
Ge 1.11109 -0.15821 0.61778
C 1.39448 -1.1216 -1.14703
H 2.44862 -1.73754 2.16751
H 2.4389 -1.47239 -1.16
C 2.42262 1.37082 0.8183
H 2.24593 1.89427 1.76664
H 2.30519 2.07827 -0.01106
H 3.44879 0.98231 0.81144
H -1.33147 -5.67296 -6.79346
C -1.76052 -6.32204 -6.01905
H -2.6652 -6.79748 -6.42012
H -1.0351 -7.11584 -5.79827
H -5.11666 -3.33001 -6.61224
H -4.67114 -5.50383 -5.74906
C -2.04989 -5.52742 -4.74763
H -3.77546 -1.49074 -5.80449
O -1.51141 -2.7398 -4.82426
N -3.01543 -4.45098 -4.95563
C -2.70053 -3.15151 -4.95425
C -5.01641 -3.32913 -5.5192
C -4.46163 -4.6868 -5.04675

H -1.13352 -5.05801 -4.36883

C -3.94363 -2.31339 -5.09474

H -2.44741 -6.18286 -3.95774

$(EP)_2PAl_{12}[Ge_B]PAl_{12}$

79

XYZ

P -0.30793 1.01073 -5.2215

Al -2.29994 1.04636 -3.52505

Al -1.52272 3.23899 -5.09541

Al -0.17476 -0.44869 -2.51503

Al -1.80486 -1.28046 -4.73506

Al 0.02227 2.29116 -2.96004

Al -2.70688 0.95945 -6.32794

Al 1.30579 3.10304 -5.34755

Al -0.37821 2.20692 -7.56603

H -6.00184 -3.11876 -5.09105

H -4.84588 -4.98071 -4.05538

H -4.14826 -1.84365 -4.11893

Al 0.8704 -1.35096 -4.87768

Al 2.0666 0.79328 -3.80154

Al -0.56466 -0.6745 -7.14333

Al 1.83783 0.61131 -6.56664

Al -1.16552 -2.31516 6.63808

Al 1.50198 -2.07253 6.51937

Al -0.03801 -1.01819 4.35044

Al 0.24944 -1.85725 9.02841

Al -2.24441 0.00403 5.81459

Al 2.06959 0.39987 5.62413

P 0.000 0.000 7.24151

Al -2.15907 -0.53899 8.57023

Al 2.32573 -0.12845 8.37057

Al -0.24981 1.69629 5.20578

Al 0.02739 0.92004 9.80139

Al -1.5711 2.02064 7.65433

Al 1.20044 2.27517 7.53596

H -2.56265 0.22434 1.11683

C -1.63656 0.81249 1.09703

H -0.97941 -2.35365 2.39043

H -1.57397 1.40681 2.01783

H -1.66221 1.4854 0.23124

H -1.00892 -2.10985 -0.72765

C -0.07152 -1.74165 2.51595

Ge -0.04349 -0.42982 0.9459
C -0.11602 -1.46557 -0.78963
H 0.78891 -2.41573 2.37607
H 0.75898 -2.13604 -0.79395
C 1.66918 0.65639 1.03634
H 1.68541 1.27095 1.94515
H 1.73216 1.3066 0.15407
H 2.53155 -0.02234 1.04567
H -2.97921 -5.86457 -6.30785
C -3.63623 -6.39031 -5.60335
H -4.53634 -6.71741 -6.14192
H -3.11263 -7.28801 -5.24953
H -6.33452 -2.93661 -6.78616
H -6.40303 -5.08676 -5.76509
C -3.9791 -5.49367 -4.41504
H -4.78748 -1.30396 -5.89583
O -2.93083 -2.85835 -4.5637
N -4.69804 -4.28329 -4.80331
C -4.14899 -3.06156 -4.82833
C -6.37072 -2.87336 -5.69047
C -6.13787 -4.26919 -5.08032
H -3.06565 -5.16925 -3.90218
C -5.1908 -2.03411 -5.17762
H -4.60445 -6.0327 -3.68648
H -7.34616 -2.46208 -5.40992
H -6.69306 -4.4191 -4.13911
H -5.42549 -1.46386 -4.26422
H 5.57079 1.56989 1.16347
C 5.57329 2.05869 0.18059
H 4.60277 2.55234 0.04465
H 6.36183 2.82329 0.18766
C 5.80388 1.01462 -0.90977
H 4.99559 0.27217 -0.90624
H 6.75602 0.48481 -0.75154
N 5.83383 1.59247 -2.25086
O 3.7859 0.8231 -2.90107
H 7.3739 3.03039 -2.05125
C 4.85393 1.45226 -3.1509
C 7.0003 2.30481 -2.78498
H 6.14199 3.99579 -3.84573
H 7.80801 1.58165 -2.99125
C 6.45853 2.96822 -4.06592
C 5.23514 2.11876 -4.44495
H 4.38152 2.68402 -4.84865
H 7.2149 3.01168 -4.85647
H 5.45973 1.33052 -5.18219

$(EP)_3PAl_{12}[Ge_B]PAl_{12}$

98

XYZ

P -0.06833 0.26195 -5.08497
Al -2.26331 0.488 -3.68549

Al -1.18557 2.53616 -5.19953
Al -0.42983 -0.99608 -2.30281
Al -1.68511 -1.89273 -4.731
Al -0.06318 1.74914 -2.75644
Al -2.25844 0.24573 -6.51746
Al 1.61152 2.32479 -4.97166
Al 0.2955 1.37862 -7.41479
Al 0.96097 -2.04591 -4.39782
Al 1.99045 0.13644 -3.21872
Al -0.02936 -1.51012 -7.00457
Al 2.26598 -0.20535 -5.98005
Al -0.73946 -2.54131 7.09549
Al 1.6937 -1.75679 6.2844
Al -0.51874 -1.21631 4.56427
Al 1.0864 -1.63457 9.0265
Al -2.46951 -0.56964 6.54001
Al 1.47346 0.70841 5.23702
P 0.000 0.000 7.3342
Al 2.50302 0.44405 7.83728
Al -1.10373 1.44138 5.39342
Al 0.45875 1.09065 9.78621
Al -1.82226 1.67707 8.09546
Al 0.7072 2.49315 7.27032
H -2.92905 0.24698 1.22422
C -1.91372 0.65849 1.17133
H -1.88567 -2.38596 2.74163
H -1.74206 1.30563 2.0426
H -1.80998 1.246 0.25168
H -1.73913 -2.36885 -0.53968
C -0.84736 -2.02128 2.79458
Ge -0.55341 -0.84493 1.14113
C -0.72664 -1.93293 -0.54771
H -0.1922 -2.90019 2.67134
H -0.0165 -2.77145 -0.45828
C 1.305 -0.02893 1.25699
H 1.35238 0.68557 2.09029
H 1.5341 0.49226 0.31832
H 2.04674 -0.82008 1.42079
H -2.79027 -6.78815 -3.45612
C -3.88284 -6.89621 -3.4388
H -4.16277 -7.73543 -4.08987
H -4.18449 -7.15232 -2.41492
H -3.1549 -5.91969 -7.82044
H -4.75256 -6.89282 -6.34866
C -4.55943 -5.59433 -3.86321
H -2.3417 -3.69832 -7.3106
O -2.88412 -3.43242 -4.61213
N -4.21138 -5.18614 -5.22002
C -3.4354 -4.12984 -5.50747
C -3.96362 -5.22162 -7.56752
C -4.80496 -5.7978 -6.41332
H -4.25868 -4.77147 -3.20233
C -3.37196 -3.92313 -6.99606
H -5.65566 -5.68967 -3.81048

H -4.56249 -5.06025 -8.46987
H -5.86876 -5.51054 -6.48131
H -3.96116 -3.02308 -7.2371
H 5.50065 -0.04703 2.04992
C 5.67172 0.49909 1.11305
H 4.93104 1.30759 1.05098
H 6.6751 0.94391 1.16321
C 5.5279 -0.45502 -0.06999
H 4.51615 -0.87854 -0.10053
H 6.24417 -1.28729 0.01278
N 5.74373 0.19287 -1.35964
O 3.57262 0.07121 -2.05896
H 7.64953 1.08095 -1.10517
C 4.77704 0.37756 -2.27417
C 7.07673 0.53375 -1.8654
H 6.78022 2.44356 -2.85717
H 7.62604 -0.3941 -2.10352
C 6.77784 1.37728 -3.11879
C 5.36441 0.94459 -3.53763
H 4.72622 1.74434 -3.93935
H 7.52589 1.22372 -3.90471
H 5.35563 0.14543 -4.29818
H -2.04562 6.43364 -2.98285
H 0.50091 6.11653 -3.51719
H -2.98236 3.67693 -1.74285
C 0.70165 5.60205 -2.56609
H 1.13126 4.62275 -2.82135
C -1.67228 6.34252 -1.94916
N -0.58694 5.35728 -1.92191
C -0.96708 4.17812 -1.41416
H -3.74572 5.97602 -1.32233
C -2.41044 4.24633 -0.98784
O -0.23516 3.14808 -1.36923
C -2.72583 5.74848 -0.99582
H -1.30596 7.32778 -1.62947
C 1.65545 6.41346 -1.692
H 2.597 6.57737 -2.23362
H -2.564 3.74627 -0.02396
H 1.24181 7.39868 -1.43422
H -2.59186 6.16555 0.01158
H 1.8836 5.87774 -0.76216
Al -1.58198 -0.86896 9.19234