

Supporting Information:

On the Making of Aromatic Organometallic Superalkali Complexes

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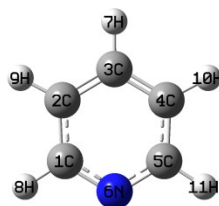
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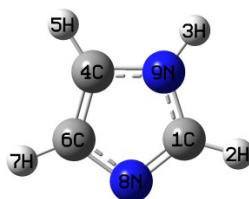
S1: Neutral Optimized geometries and Cartesian Coordinates of Pyridine and Imidazole, Au₃, Au₃L₁ and Au₃L₃ (L : IMD, Py)

Pyridine (Py)



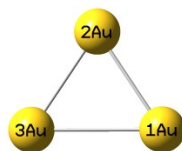
C	-1.13471500	-0.71823000	-0.00019700
C	-1.19067400	0.66824200	-0.00011700
C	-0.00002100	1.37628400	0.00008400
C	1.19065300	0.66828000	0.00021000
C	1.13473700	-0.71819300	0.00010500
N	0.00002200	-1.40933300	-0.00009800
H	-0.00004400	2.46061100	0.00015700
H	-2.05084700	-1.30310900	-0.00036700
H	-2.14773400	1.17626200	-0.00020800
H	2.14770200	1.17632000	0.00039000
H	2.05088600	-1.30304600	0.00020300

Imidazole (IMD)

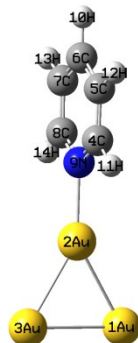


C	0.97719200	-0.54488100	0.00000400
H	1.96961900	-0.97063700	0.00000500
H	1.46013900	1.51117300	0.00000600
C	-0.59662600	0.98420600	-0.00000400
H	-1.04007700	1.96580700	-0.00000600
C	-1.13302400	-0.27140200	0.00000700
H	-2.17654900	-0.54596400	0.00001000
N	-0.14418600	-1.21613100	-0.00000800
N	0.75870300	0.79214300	-0.00000100

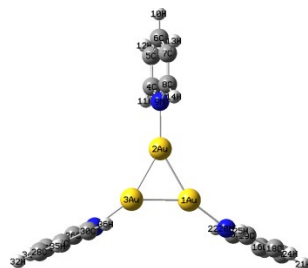
Au₃



Au	1.45541600	-0.72350100	0.00000000
Au	0.00000000	1.44699100	0.00000000
Au	-1.45541600	-0.72349000	0.00000000

Au₃(Py)₁

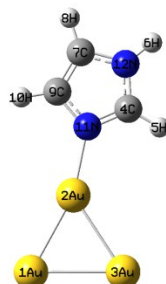
Au	-1.51232900	1.35815500	0.00010900
Au	0.76159800	-0.00092800	-0.00023600
Au	-1.51344000	-1.35729500	0.00003300
C	3.54303900	0.00006300	-1.15048300
C	4.92359300	0.00054800	-1.19028900
C	5.63172200	0.00059800	0.00032900
C	4.92332900	0.00016400	1.19079000
C	3.54278300	-0.00030100	1.15067500
N	2.85798600	-0.00035200	0.00001900
H	6.71521200	0.00096700	0.00044900
H	2.95339300	0.00002400	-2.05822200
H	5.42786100	0.00087500	-2.14815500
H	5.42738400	0.00018700	2.14876800
H	2.95293800	-0.00066900	2.05828300

Au₃(Py)₃

Au	1.39615600	-0.63188300	-0.00396300
Au	-0.11704700	1.50837700	0.00357700
Au	-1.27845200	-0.84058700	0.00187700
C	-0.32611900	4.29328600	-1.15234900
C	-0.44076400	5.66269400	-1.18898800
C	-0.51394100	6.38317500	0.00245800
C	-0.46562800	5.66105800	1.19416200
C	-0.35016800	4.29160900	1.15794300
N	-0.27964800	3.58950400	0.00287700
H	-0.60469700	7.46177100	0.00219000
H	-0.26754300	3.71147800	-2.06339900
H	-0.47225800	6.16146700	-2.15008900
H	-0.51734100	6.15838600	2.15513700
H	-0.31035200	3.70834100	2.06905600
C	3.91464900	-1.87795400	-1.15237800
C	5.21664200	-2.32556700	-1.16919200
C	5.84684000	-2.64473700	0.03039200
C	5.11446600	-2.50428500	1.20594600
C	3.81581600	-2.05100300	1.14532700
N	3.20702700	-1.73022800	-0.01442300
H	6.87176700	-2.99351000	0.04834000
H	3.39629600	-1.62416600	-2.06875700

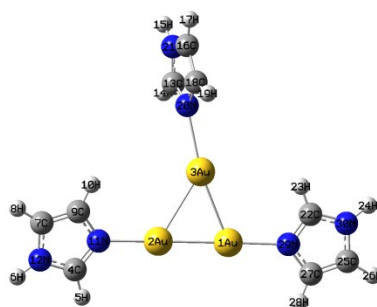
H	5.72870300	-2.42710000	-2.11820400
H	5.54433300	-2.74990900	2.16931500
H	3.21925800	-1.93468600	2.04163100
C	-3.47675100	-2.57914000	-1.15730100
C	-4.68760500	-3.23222800	-1.21108000
C	-5.36225100	-3.52344400	-0.02861600
C	-4.76509000	-3.14299900	1.16991300
C	-3.55159600	-2.49282700	1.14606700
N	-2.90117100	-2.20068600	0.00193300
H	-6.31843000	-4.03134500	-0.04076100
H	-2.92709700	-2.34030600	-2.05924500
H	-5.09416900	-3.51369800	-2.17475800
H	-5.23371100	-3.35298500	2.12355800
H	-3.06113300	-2.18635100	2.06165900

Au₃(IMD)₁



Au	-1.53949000	1.23616700	0.00006700
Au	0.87381800	0.25904100	0.00003200
Au	-1.22853500	-1.46515400	-0.00010100
C	3.61438700	-1.05956900	0.00066900
H	3.17070400	-2.04171700	0.00130500
H	5.65328800	-1.52922100	0.00064700
C	5.13444900	0.53014200	-0.00049500
H	6.11593400	0.97181000	-0.00088600
C	3.89161000	1.08257700	-0.00063200
H	3.60608700	2.12049100	-0.00118800
N	2.95699700	0.07949200	0.00010900
N	4.93638800	-0.82442300	0.00032700

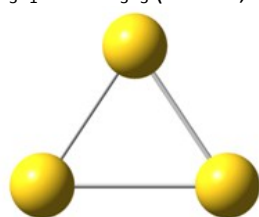
Au₃(IMD)₃



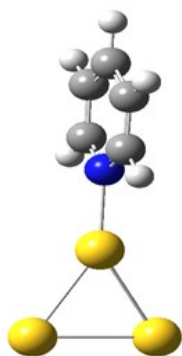
Au	-1.46353500	0.99240800	-0.03237900
Au	1.04026700	1.37132100	-0.02193500
Au	0.02517600	-1.30565900	0.06395900
C	3.77571600	2.86846500	-0.17365500
H	3.28001200	3.79833900	-0.40102300
H	5.78715000	3.46743600	-0.15011700
C	5.37699200	1.42047200	0.24426000
H	6.37846200	1.05483000	0.39471300
C	4.16399500	0.80266300	0.28472300
H	3.92723800	-0.22924400	0.48367300
N	3.17957700	1.71757000	0.02246700
N	5.11027200	2.73201200	-0.04868100

C	1.30755300	-4.13939600	-1.09210000
H	1.34056100	-3.69444500	-2.07460000
H	1.94250100	-6.10230500	-1.51733300
C	1.47297600	-5.64171200	0.50296900
H	1.67276300	-6.59642000	0.96049400
C	1.04110900	-4.45199800	1.01025200
H	0.79249600	-4.19935000	2.02863100
N	0.94423800	-3.53007800	0.00643100
N	1.63826300	-5.42454700	-0.83975100
C	-4.15594600	-0.49974000	0.13564200
H	-3.60704400	-1.42183600	0.24650900
H	-6.14335900	-1.16687800	0.22220900
C	-5.82895500	0.91889000	-0.03401500
H	-6.84955400	1.25935100	-0.07286100
C	-4.64215200	1.58146400	-0.11738400
H	-4.45678900	2.63465200	-0.24572100
N	-3.61315600	0.68574400	-0.01018900
N	-5.49960200	-0.40160900	0.12677100

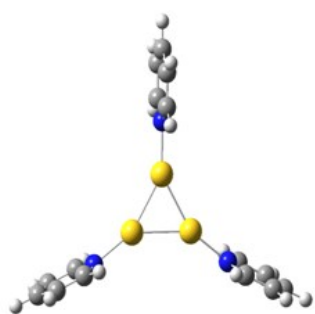
S2: Optimised Neutral structures of Au_3 , Au_3L_1 and Au_3L_3 (L : IMD, Py)



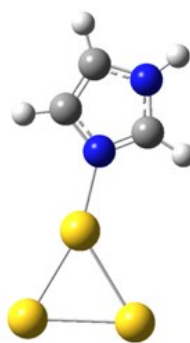
$Au_3:C_{2v}$



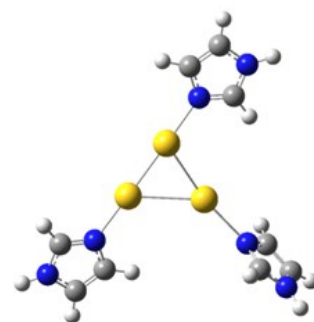
$Au_3(Py)_1:C_{2v}$



$Au_3(Py)_3:C_1$



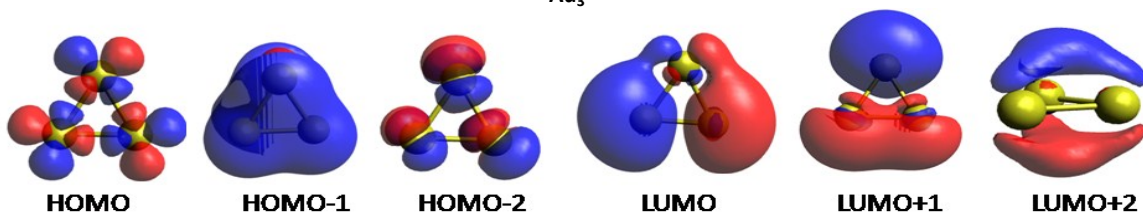
$Au_3(IMD)_1:C_s$



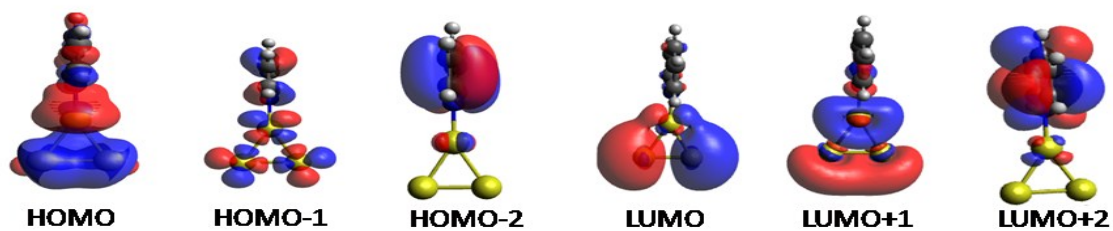
$Au_3(IMD)_3:C_1$

S3: Molecular Orbitals of Au_3^+ , Au_3L_1^+ and Au_3L_3^+ (L : IMD, Py)

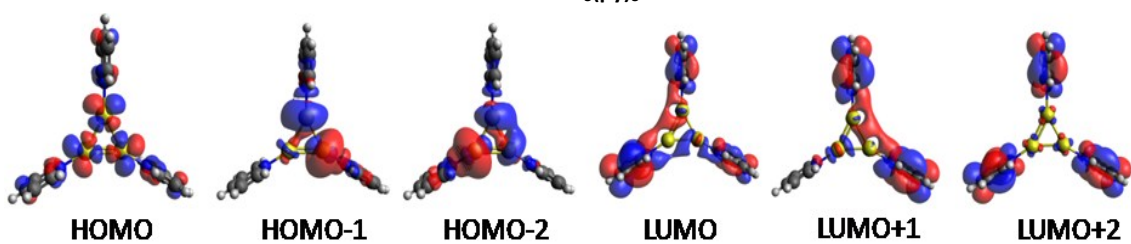
Au_3^+



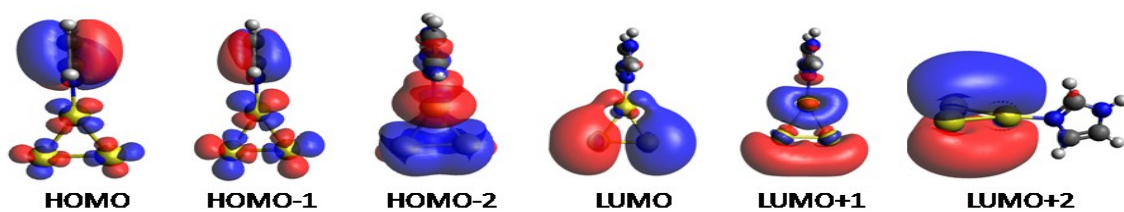
$\text{Au}_3(\text{py})_1^+$



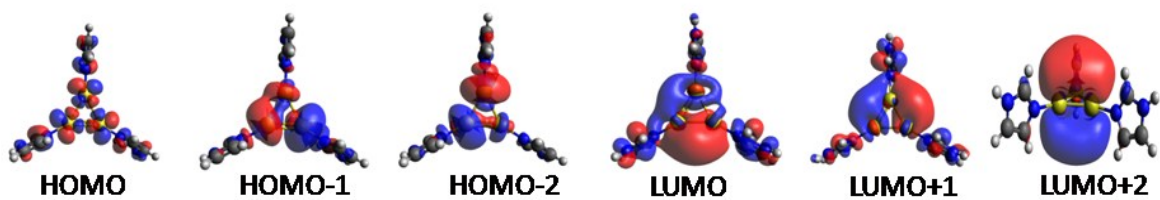
$\text{Au}_3(\text{py})_3^+$



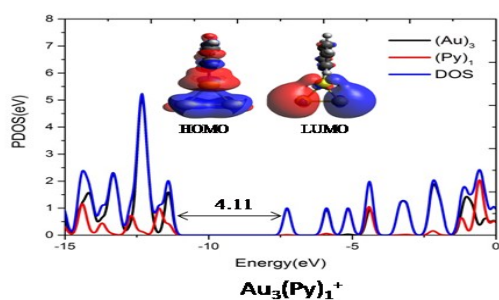
$\text{Au}_3(\text{IMD})_1^+$



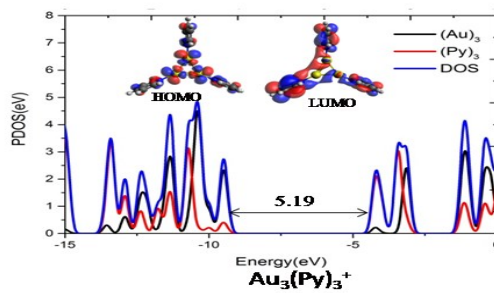
$\text{Au}_3(\text{IMD})_3^+$



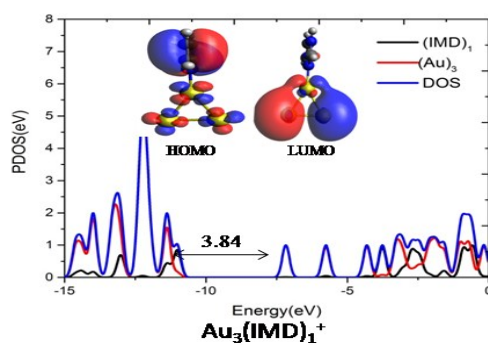
S4: DOS of Ligand substituted triatomic molecule $Au_3L_1^+$ and $Au_3L_3^+$ (L : IMD, Py)



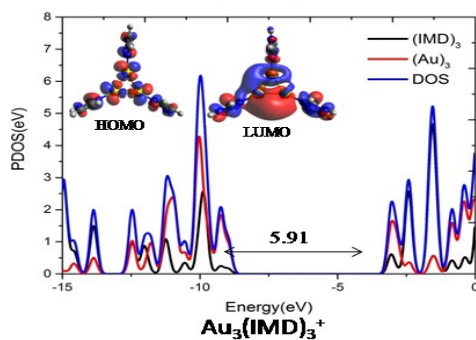
	Au_3	$(Py)_1$
L+5	99	1
L+4	94	6
L+3	0	100
L+2	3	97
L+1	94	6
LUMO	99	1
HOMO	74	26
H-1	87	13
H-2	2	98
H-3	100	0
H-4	100	0
H-5	94	6



	$(Au)_3$	$(Py)_3$
L+5	0	100
L+4	0	100
L+3	0	100
L+2	2	98
L+1	11	89
LUMO	11	89
HOMO	87	13
H-1	84	16
H-2	84	16
H-3	79	21
H-4	95	5
H-5	97	3



	$(Au)_3$	$(IMD)_1$
L+5	72	28
L+4	99	1
L+3	8	92
L+2	96	4
L+1	95	5
LUMO	99	1
HOMO	15	85
H-1	75	25
H-2	82	18
H-3	101	0
H-4	100	0
H-5	98	2



	$(Au)_3$	$(IMD)_3$
L+5	18	82
L+4	17	83
L+3	2	98
L+2	91	9
L+1	70	30
LUMO	70	30
HOMO	84	16
H-1	88	12
H-2	88	12
H-3	90	10
H-4	35	65
H-5	34	66

S5: Non linear optical property Au_3 , Au_3L_1 and Au_3L_3 (L : IMD, Py) by Different level of theory.

Molecules	PBE1PBE/Def2tzvp		CAM-b3lyp/Def2tzvp		M062X/SDD	
	Dipole moment (Debye)	Static First order hyperpolarizability (esu)	Dipole moment (Debye)	Static First order hyperpolarizability (esu)	Dipole Moment (Debye)	Static First order hyperpolarizability (esu)
Au_3	0.998	10.871×10^{-30}	1.355	26.572×10^{-30}	0.926	2.162×10^{-30}
$Au_3(Py)_1$	8.744	107.635×10^{-30}	9.048	24.961×10^{-30}	9.219	34.421×10^{-30}
$Au_3(Py)_3$	1.250	322.979×10^{-30}	4.416	$20213.012 \times 10^{-30}$	2.577	4582.949×10^{-30}
$Au_3(IMD)_1$	10.354	11.258×10^{-30}	10.37	13.865×10^{-30}	10.745	14.965×10^{-30}
$Au_3(IMD)_3$	5.830	37.586×10^{-30}	6.101	6.671×10^{-30}	6.711	24.187×10^{-30}

S6: Binding Energy Au_3L_1 and Au_3L_3 (L : IMD, Py)

Molecules	Binding Energy (Kcal/mol)
$Au_3(Py)_1$	-31.652
$Au_3(Py)_3$	-56.869
$Au_3(IMD)_1$	-33.939
$Au_3(IMD)_3$	-51.02

S7: Some Important Bond distances and bond angles of Au_3 , Au_3L_1 and Au_3L_3 (L : IMD, Py) (For Neutral and Cation Geometry).

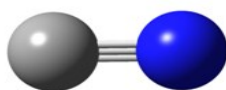
Systems	Neutral			Cation		
	Bond Distances Between Au of Au_3 (A°)	Bond Distance between Au of Au_3 and N of Ligand (A°)	Bond Angles Between Au of Au_3 (In degree)	Bond Distances Between Au of Au_3 (A°)	Bond Distance between Au of Au_3 and N of Ligand (A°)	Bond Angles Between Au of Au_3 (In degree)
Au_3	2.61, 2.61, 2.91		56.15, 56.15, 67.68	2.64, 2.64, 2.64		60.0, 60.0, 60.0
$Au_3(Py)_1$	2.65, 2.65, 2.71	2.09	59.16, 59.17, 61.67	2.58, 2.67, 2.67	2.08	57.74, 61.12, 61.13
$Au_3(Py)_3$	2.62, 2.62, 2.68	2.09, 2.09, 2.11	59.20, 59.22, 61.57	2.63, 2.63, 2.63	2.12, 2.12, 2.12	60.0, 60.0, 60.0
$Au_3(IMD)_1$	2.60, 2.72, 2.72	2.09	58.42, 60.79, 60.79	2.58, 2.67, 2.67	2.06	57.79, 61.11, 61.11
$Au_3(IMD)_3$	2.56, 2.73, 2.86	2.17, 2.17, 2.40	53.67, 60.65, 65.67	2.63, 2.63, 2.63	2.10, 2.10, 2.10	60.0, 60.0, 60.0

S8: Vertical Ionisation Energies of studied Ligands and Complexes with Optimized Geometries calculated at PBE/Def2-TZVP level of theory

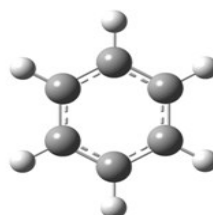
Molecules	Vertical Ionisation Energy (VIE) (eV)
C ₆ H ₆	9.27
CH ₃	9.96
CN	15.21
Py	9.47
IMD	8.90
Au ₃ (C ₆ H ₅) ₃	8.04
Au ₃ (CH ₃) ₃	8.25
Au ₃ (CN) ₃	11.54
Au ₃ (Py) ₁	5.84
Au ₃ (Py) ₃	3.38
Au ₃ (IMD) ₁	8.90
Au ₃ (IMD) ₃	3.42



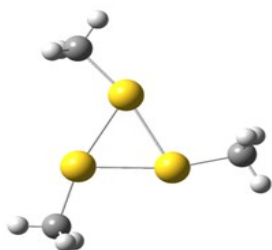
CH₃



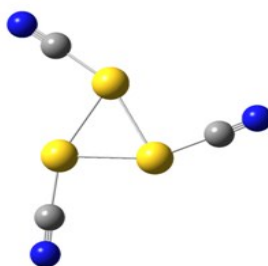
CN



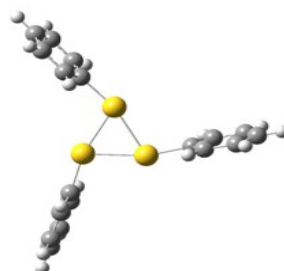
C₆H₆



Au₃(CH₃)₃



Au₃(CN)₃



Au₃(C₆H₅)₃

