Supporting Information

Theoretical investigation of the valence states in Au via the Au-F compounds under high pressure

The formation enthalpy ($H_{f/atom}$) of each stoichiometric phase is defined as:

$$H_{f/atom} = \frac{H_{AuF_x/f.u.} - H_{Au/atom} - x\,H_{F/atom}}{1+x}$$

where we use the *Fm*-3*m* structure for Au[1] and the *C*2/*m* or *C*2/*c* structures for F_2[2] as the endpoints at the appropriate pressures.

[1] P. M. Bell, J. Xu, H. K. Mao, *In Shock Waves in Condensed Matter,Ed. Y. M Gupta, Plenum*, New York, **1986**.

[2] L. Pauling, I. Keaveny, A. B. Robinson, *J. Solid State Chem.* **1970**, *2*, 225–227.

Parameter Convergence Test

a) Energy cutoff test at selected pressures.

Energy cutoff (eV)	AuF, Energy (eV/atom)	AuF_2, Energy (eV/atom)	AuF_3, Energy (eV/atom)
400	-2.9414	-2.8865	-2.9411
500	-2.9364	-2.8793	-2.9303
600	-2.9372	-2.8807	-2.9320
700	-2.9379	-2.8824	-2.9338
800	-2.9384	-2.8830	-2.9343
1000	-2.9384	-2.8830	-2.9343
1200			-2.9345

We set energy cutoff with 700 eV in structural optimization, enthalpy and electronic structure calculations.

b) Monkhorst-Pack grid test at selected pressures.

Monkhorst-Pack grid	AuF, Energy (eV/atom)	AuF_2, Energy (eV/atom)	AuF_3, Energy (eV/atom)
1.0			-2.9291
0.8	-2.9845	-2.8635	-2.9312
0.5	-2.9372	-2.8814	-2.9320
0.4	-2.9306	-2.8819	-2.9320
0.3	-2.9234	-2.8803	-2.9320
0.2	-2.9288	-2.8819	-2.9320
0.15	-2.9281	-2.8821	

Theoretical Method Test

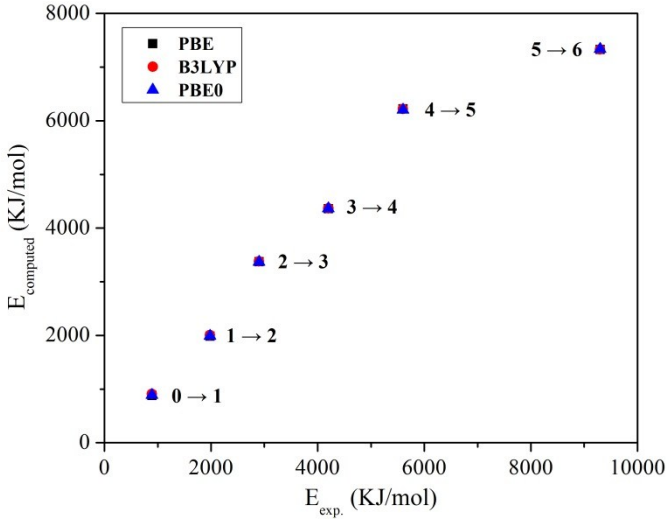
Lattice parameters of AuF_3 at ambient pressure.

	parameters (Å)
Exp.	a = 5.151, c = 16.264
PBE	a = 5.324, c = 16.554
PBEsol	a = 5.127, c = 16.396
Vdw	a = 5.037, c = 16.619
LDA	a = 4.869, c = 16.317

Enthalpies/lattice parameters of AuF_2 with PBE and PBEsol functionals at 15 GPa. And the energy sequences of AuF_2 are same with different functionals.

Phase		PBE	PBEsol
$P2_1/c$	H (eV/f.u.)	-5.529	0.057
	Lattice (Å)	a = 2.908, b = 5.933, c =5.134, β = 125.7°	a = 2.822, b = 5.931, c = 5.034, β = 125.9°
Cmcm	H (eV/f.u.)	-5.592	-0.043
	Lattice (Å)	a = 5.144, b = 6.237, c = 4.300	a = 5.048, b = 6.172, c = 4.221
Pnma	H (eV/f.u.)	-5.632	-0.084
	Lattice (Å)	a = 4.203, b = 5.424, c = 6.149	a = 4.124, b = 5.320, c = 6.101

We compared the ionization energy for Au^{+n} (n=0, 1, 2, 3, 4, 5, and 6) using PBE PBE0 B3LYP functional and SK-MCDHF-RSC basis set. The relativistic kinetic energy is considered with ZORA implemented in orca quantum chemistry program (https://orcaforum.cec.mpg.de). The corresponding ionization energies are given in the following figure. Our tests show that PBE, B3LYP, and PBE0 give similar ionization energy and the computed ionization energies agree with the experimental values. For example, from Au^0 to Au^{+1}, the ionization energies are 880.5 KJ/mol (PBE), 909.8 KJ/mol (B3LYP), 890.2 KJ/mol (PBE0), and 890.1 KJ/mol (experiment, http://http//www.freshney.org). Considering these ionization energies, the results of PBE should be sufficient to describe the Au complexes.



The calculated lattice parameters of the ambient AuF_3 phase were compared with different theory levels. The PBE and PBEsol methods give better results. It is normal that PBEsol improves on PBE for equilibrium properties, but typically is worse for dissociation or cohesive energies. The formation energy of AuF_6 was tested between PBE and PBEsol, and they produced similar conclusion. Therefore, we mainly adopted PBE GGA functional during the study.

Figures and captions:

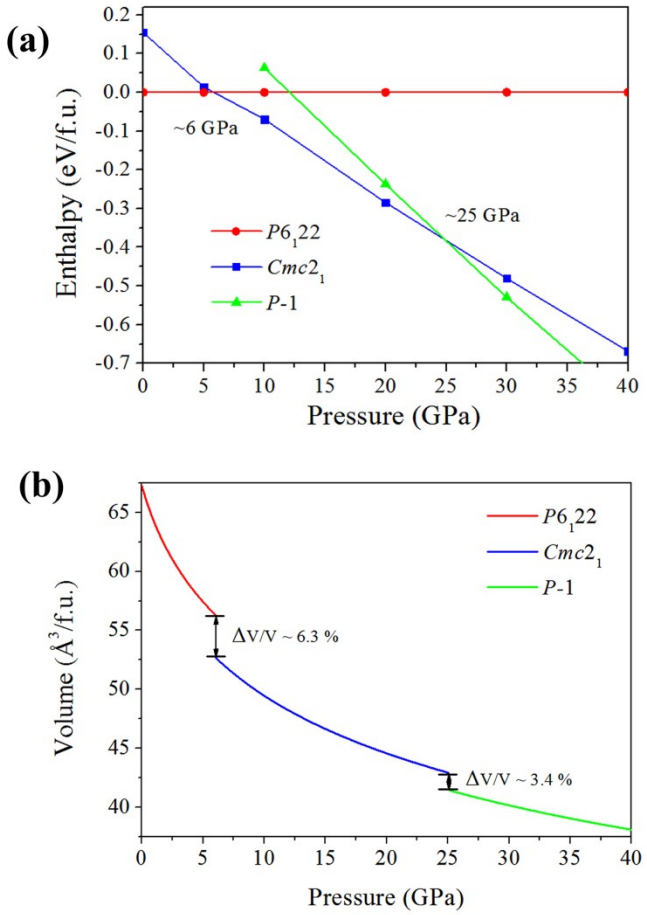


Figure S1: The calculated (a) enthalpy and (b) volume as a function of pressure forAuF_3.

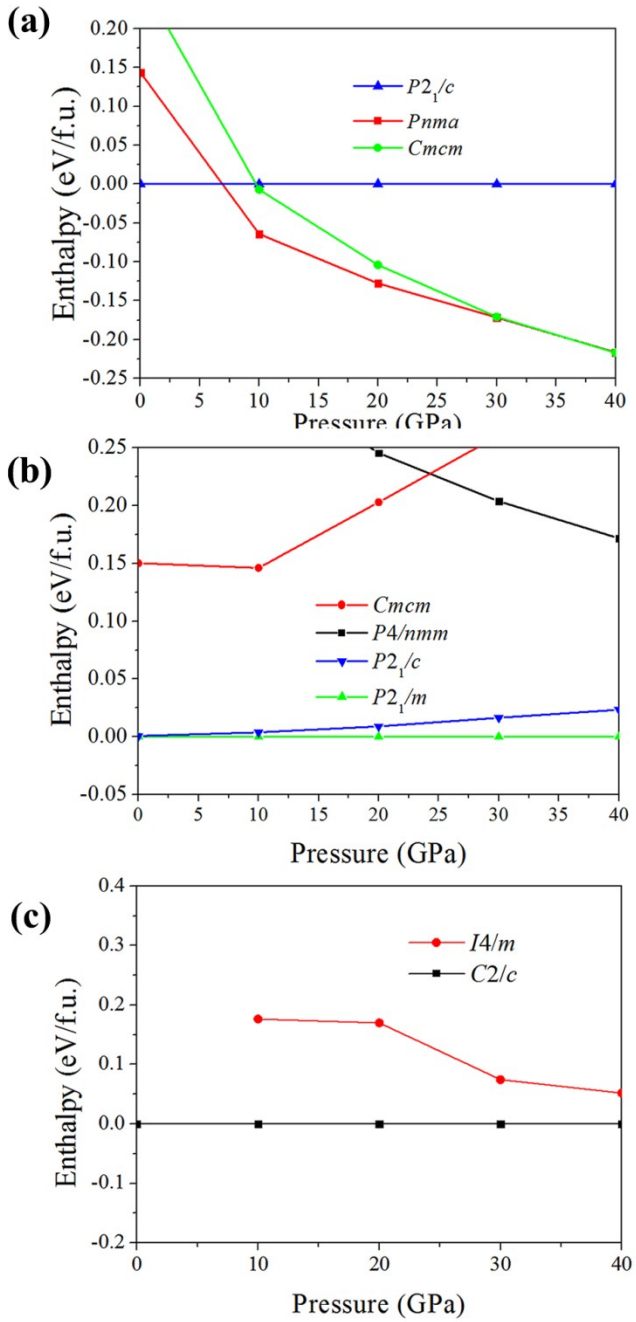


Figure S2: The calculated enthalpy as a function of pressure for (a) AuF_2, (b) AuF and (c) AuF_4.

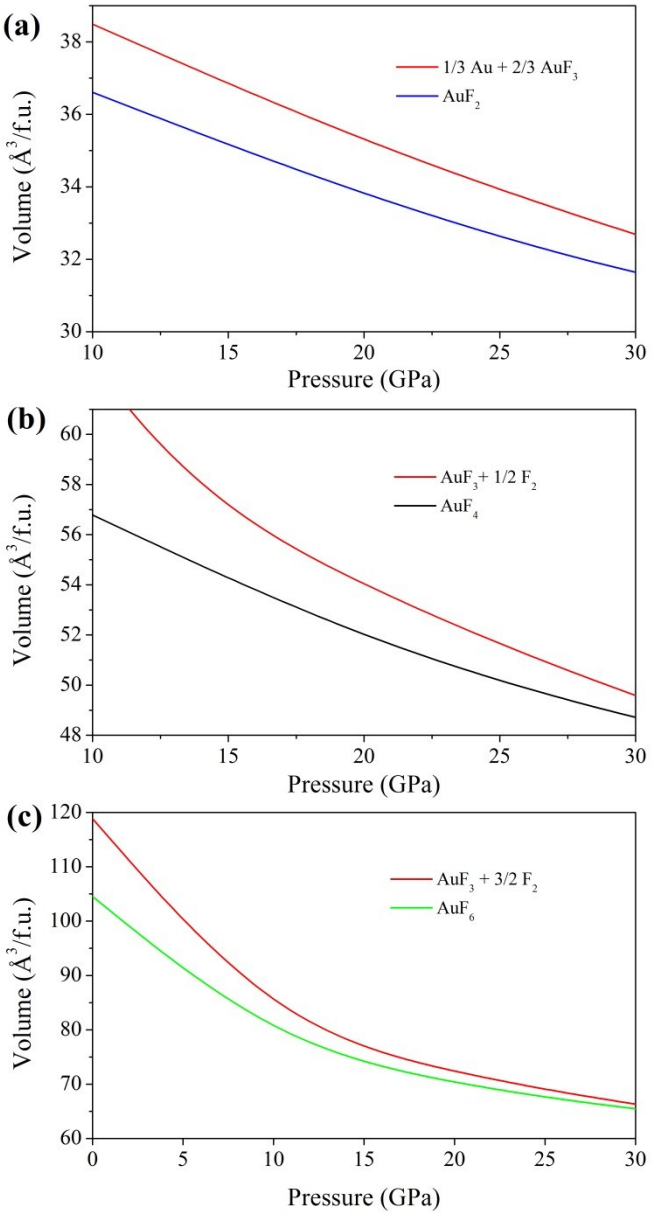


Figure S3: The equations of state of (a) AuF_2, (b) AuF_4 and (c) AuF_6 compared with their reactants.

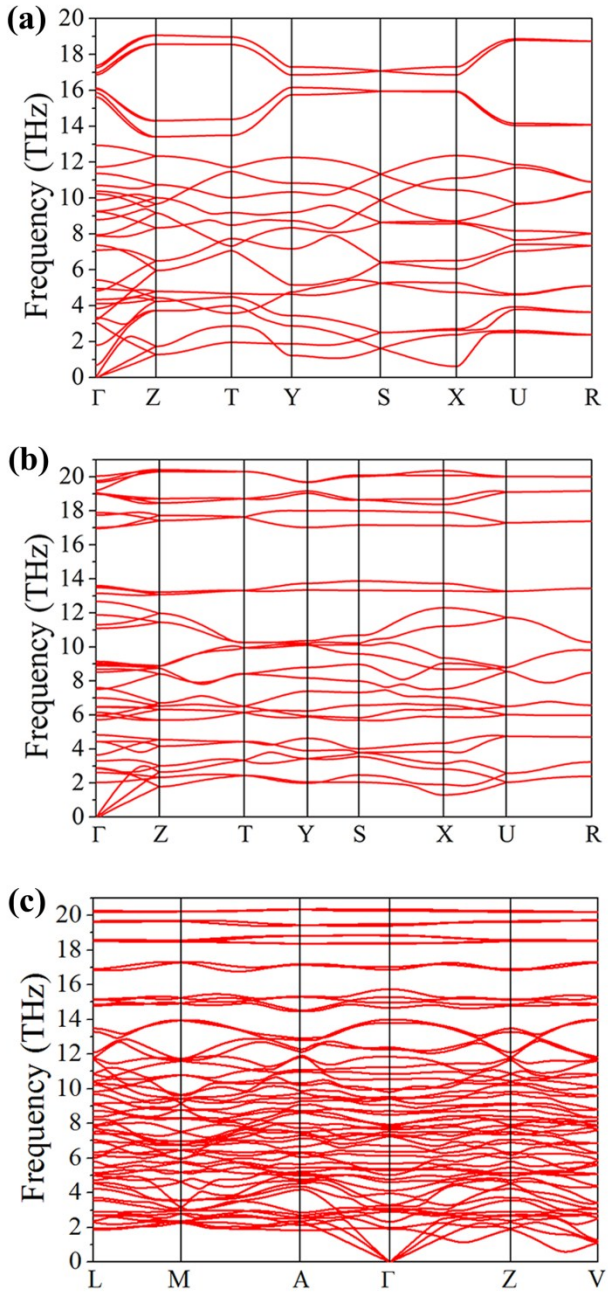


Figure S4: The phonon dispersions curve of (a) AuF_2 (*Pnma*) phase, (b) the AuF_3 ($Cmc2_1$) phase and (c) the AuF_4 ($C2/c$) phase.

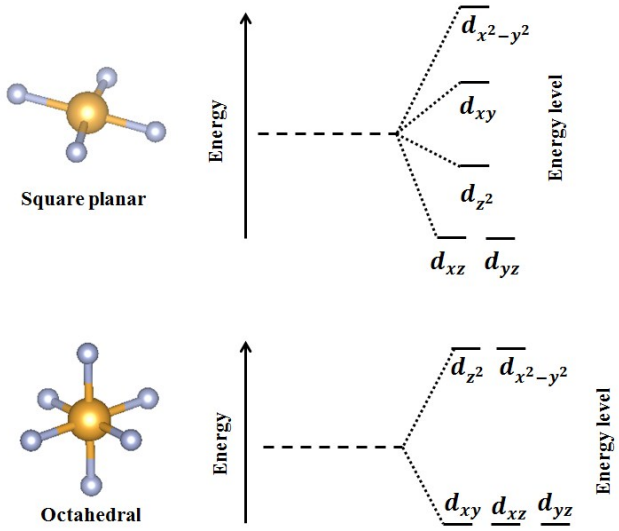


Figure S5: The crystal field splitting diagrams of square planar and octahedral geometries.

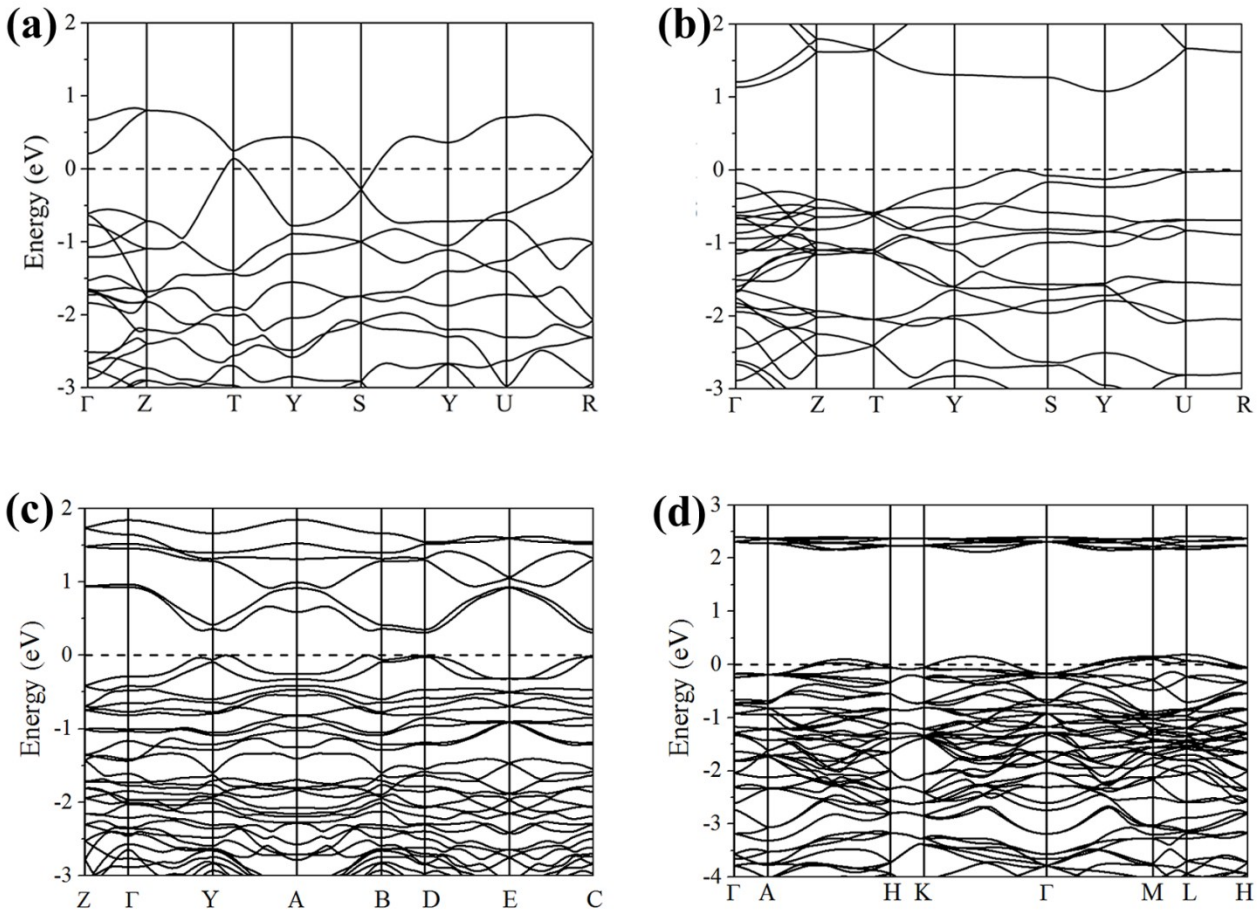


Figure S6: Figure 5: Band structures along high symmetry paths of (a) the *Pnma* phase (AuF_2), (b) the *Cmc*2_1 phase (AuF_3), (c) the *C*2/*c* phase (AuF_4) and (d) the *R*-3 phase (AuF_6). The Fermi level has been set to 0 eV.

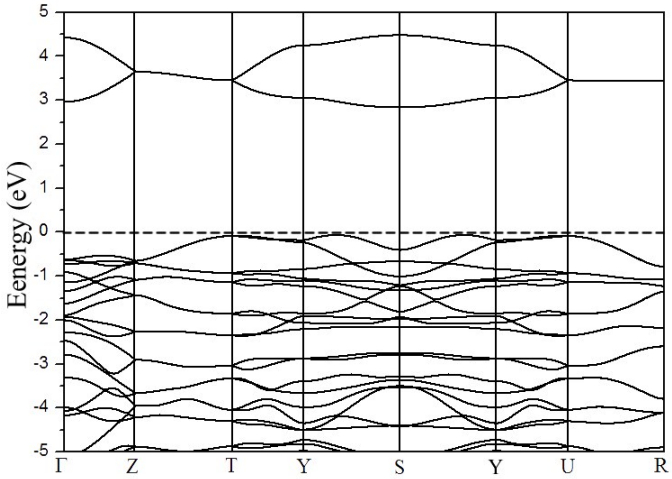


Figure S7: The band structure of the *Cmc*2_1 phase (AuF_3) calculated with the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06). The Fermi level has been set to 0 eV.

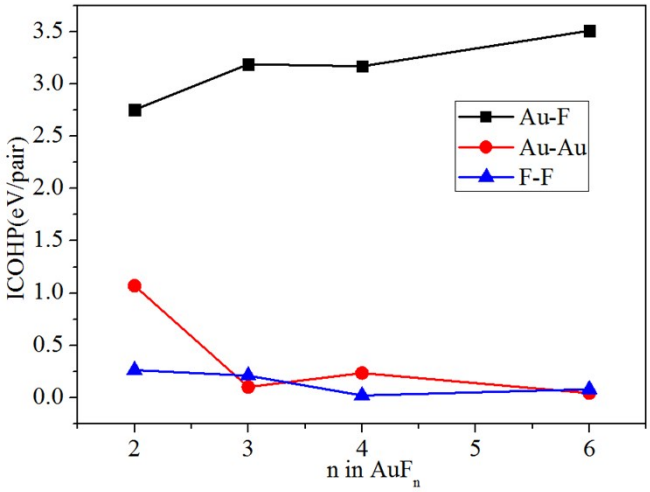


Figure S8: The calculated integrated crystal orbital Hamiltonian populations (ICOHP) for Au-F, Au-Au and F–F pairs in AuF_n compounds at 20 GPa.

Table. The calculated crystal structure data of AuF_n.

Space group	Pressure (GPa)	Lattice parameters (Å)	Atoms	*x*	*y*	*z*
$P2_1c$ (AuF)	10	*a* = 2.930 *b* = 11.049 *c* = 4.465 *β* = 130.84°	Au F	0.3835 0.0799	0.4219 0.1874	0.7497 0.7493
$P2_1/m$ (AuF)	10	a = 2.923 b = 3.374 c = 5.5272 *β* = 85.48°	Au F	0.3850 0.2120	0.75 0.25	0.8438 0.6253
$P2_1/c$ (AuF_2)	0	*a* = 4.267 *b* = 5.536 *c* = 6.399 *β* = 136.85°	Au F	1.0650 0.5	0.2893 0.5	0.3678 0
Pnma (AuF_2)	10	a = 5.2545 b = 4.172 c = 6.152	Au F(1) F(2)	0.8492 0.4126 0.1966	0.25 0.25 0.75	0.0369 0.1485 0.2776
$P6_122$ (AuF_3)	0	*a* = 5.320 *b* = 16.559	Au F(1) F(2)	0.4766 0.1647 0.7695	0.2383 0 0.3093	0.0833 0 0.0046
$Cmc2_1$ (AuF_3)	20	*a* = 4.430 *b* = 7.397 *c* = 5.455	Au F(1) F(2) F(3)	0 0 0 0	0.3335 0.1003 0.2155 0.4251	0.4923 0.3377 0.8033 0.1460
*C*2/*c* (AuF_4)	20	*a* = 7.978 *b* = 6.702 *c* = 12.430 *β* = 141.35°	Au(1) Au(2) F(1) F(2) F(3) F(4)	0.75 0.75 0.7602 0.7411 0.4842 0.0117	0.75 0.75 0.7953 0.7853 0.9887 0.9836	0.5 0 0.8538 0.3435 0.5965 0.3591