Electronic Supplementary Material (ESI) for Chemical Communications.
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Supporting Information:

Table S1. Au_a-Au_b distance part of SR-Au-SR linear motif and dihedral values in S-Au-Au-S including relaxed energy values.

Temp. (K)	Isomer numbers as labeled in Fig. 2	Dihedral angle [°] S-Au- Au -S	Distance [Å] Au_a-Au_b	Relaxed energy [eV]
-	Static crystal structure	89.3	4.74	0
145	1	100.4	3.62	−0.40
145	2	101.6	3.83	−0.42
280	3	103.6	3.60	−0.32
280	4	99.4	3.75	−0.33
280	5	100.4	3.78	−0.35
475	6	94.7	3.83	−0.19
475	7	106.6	3.51	−0.33

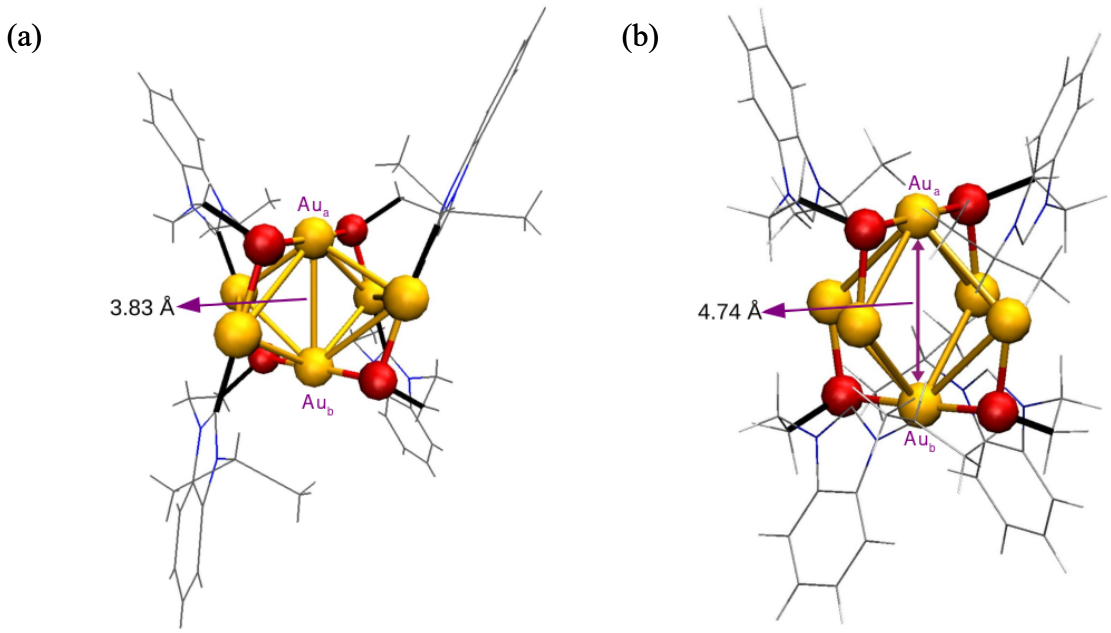

Fig. S1 (a) Optimized structure of isomer 2, (b) optimized structure of static single crystal structure. The Au-Au distance in isomer 2 is 3.83 Å and dihedral angle value is 101.6°, the Au_a-Au_b distance in single crystal structure is 4.74 Å and dihedral angle is 89.3°.

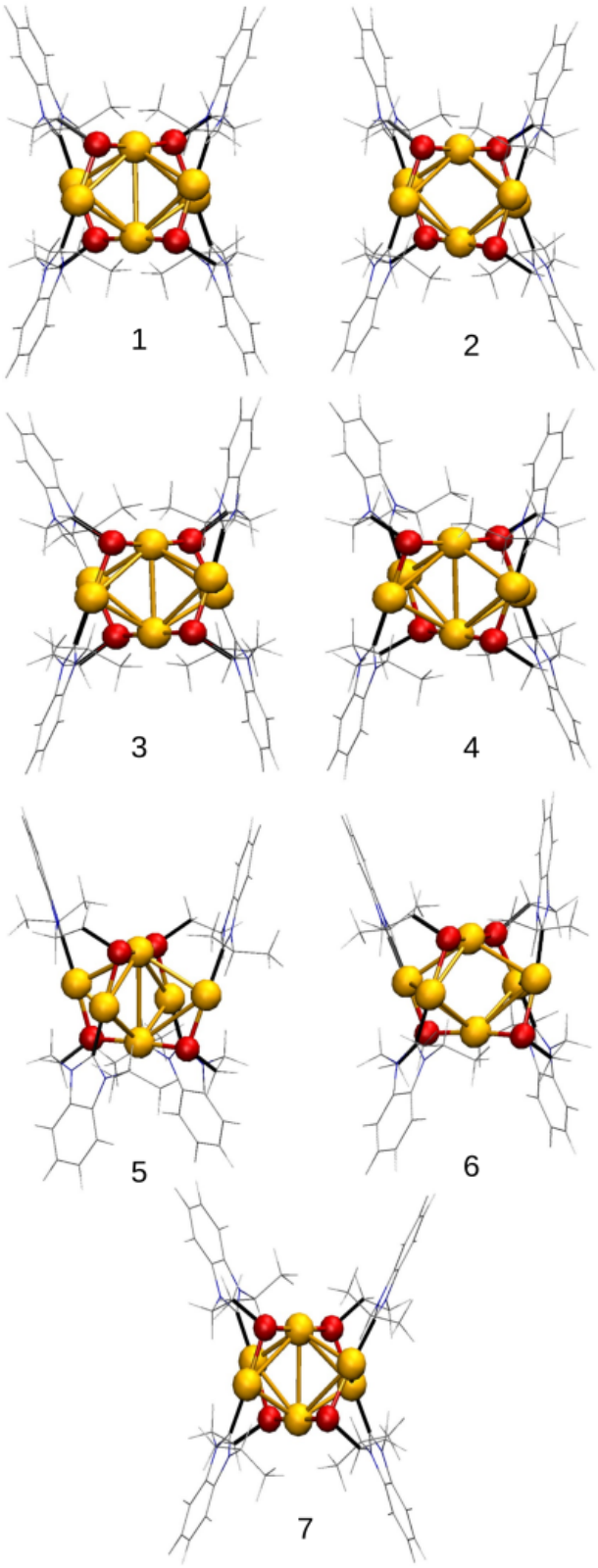

Fig. S2 Isomer structures found in DFT-MD (145 K, 280 K and 475 K), labled 1 to 7. The isomer number 2 has been found the most stable cluster. During the isomer transition, no bonds were broken. Au_a-Au_b distance (as labled in Fig. S1) varies between 3.51 Å and 3.83 Å; these variations, together with differences in dihedral angle (94.7°-106.6°), reflect the structural alterations of the stated isomers.

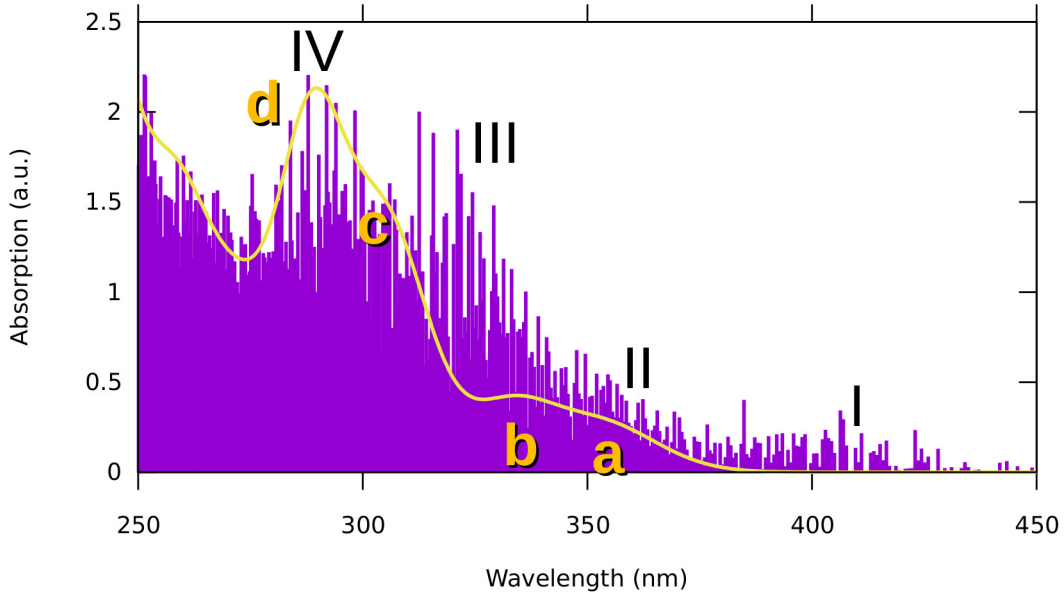

Fig. S3 Optical absorption spectra in 280 K as combined from 50 snapshot structures (purple lines) chosen in every 65 steps compared to static single crystal structure (yellow curve). Spectrum for the dynamic structures is shown as a stick spectrum including all single particle transitions and their oscillator strengths from the 50 structures that are collected into energy bins. The spectrum for optimized static crystal structure is broadened by 0.1 ev Gaussians.

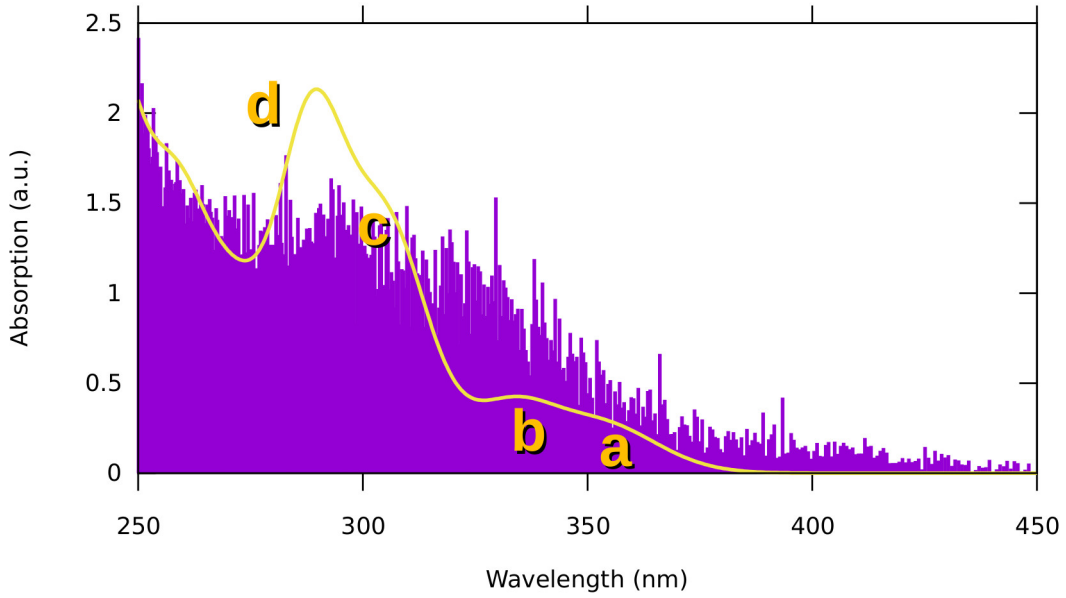

Fig. S4 Optical absorption spectra in 475 K as combined from 120 snapshot structures (purple lines) chosen in every 65 steps compared to static single crystal structure (yellow curve). Discrete peaks oscillator strengths are not visible at 475 K, as they are in 145 K and 280 K.

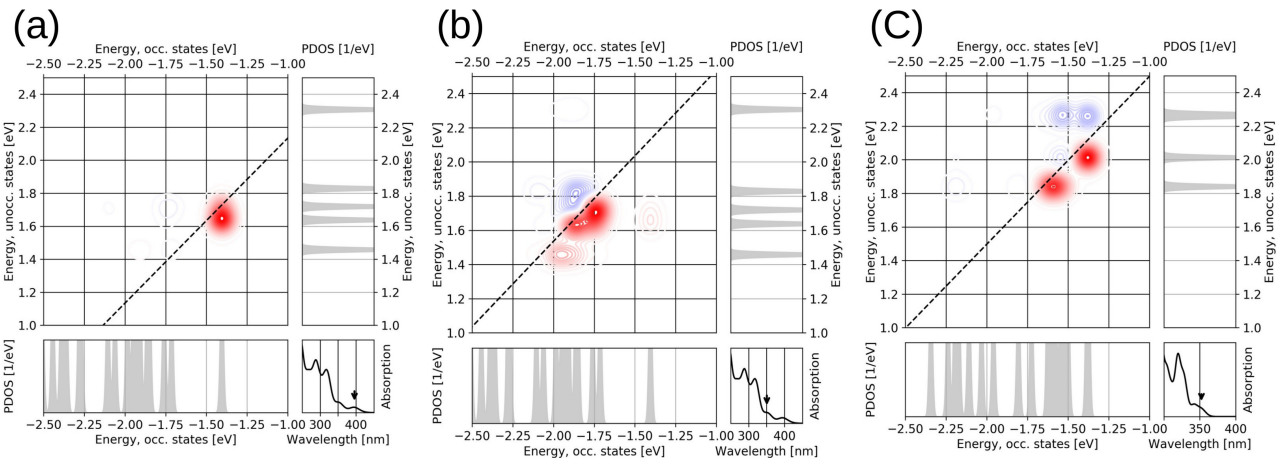

Fig. S5 DTCM for the chosen dynamic structure (a: peak I and b: peak II) comparing to DTCM for the first peak of relaxed crystal structure (c) showing strengthening and screening contributions in red and blue, respectively, for the selected absorption peak that is labeled with the spectrum in the lower right panel. The occupied and the unoccupied electron states are shown in the bottom left sub-plot and on the right vertical sub-plot, respectively.

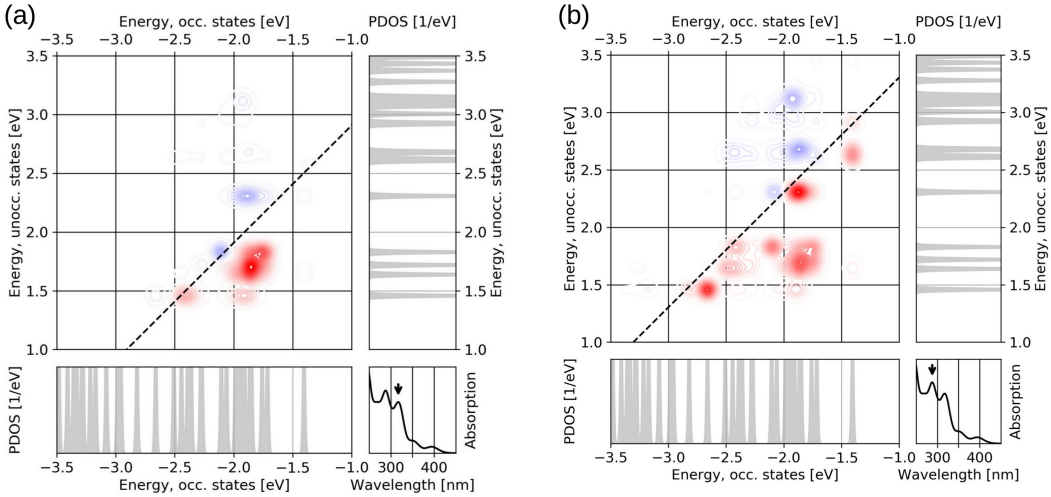

Fig. S6 DTCM for the chosen dynamic structure showing strengthening and screening contributions in red and blue respectively for the selected absorption peak that is labeled with the spectrum in the lower right panel (a) peak III (b) peak IV. The occupied and the unoccupied electron states are shown in the bottom left sub-plot and on the right sub-plot, respectively.

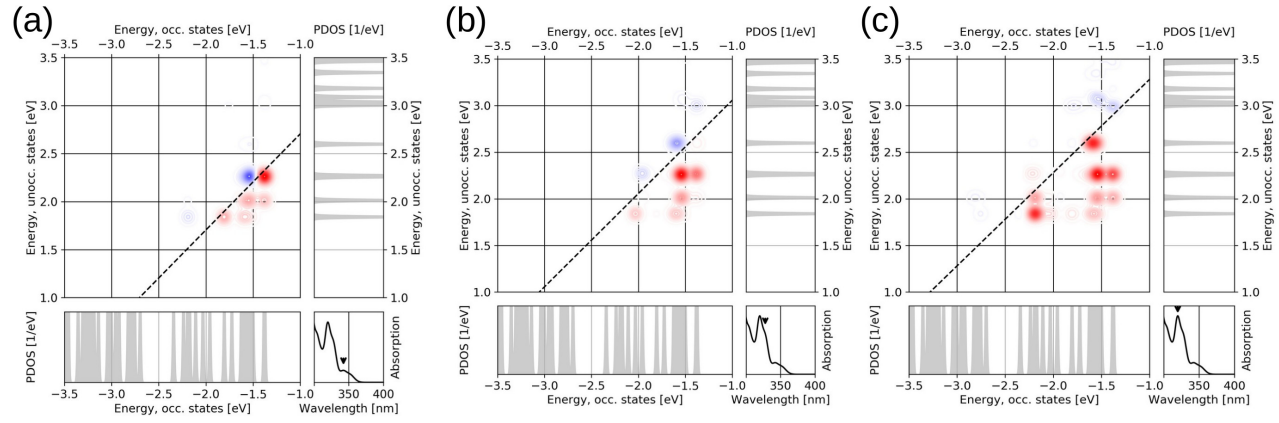

Fig. S7 The same as in Fig. S6 but the peaks second, third and fourth for relaxed crystal structure in (a), (b) and (c) panels, respectively.

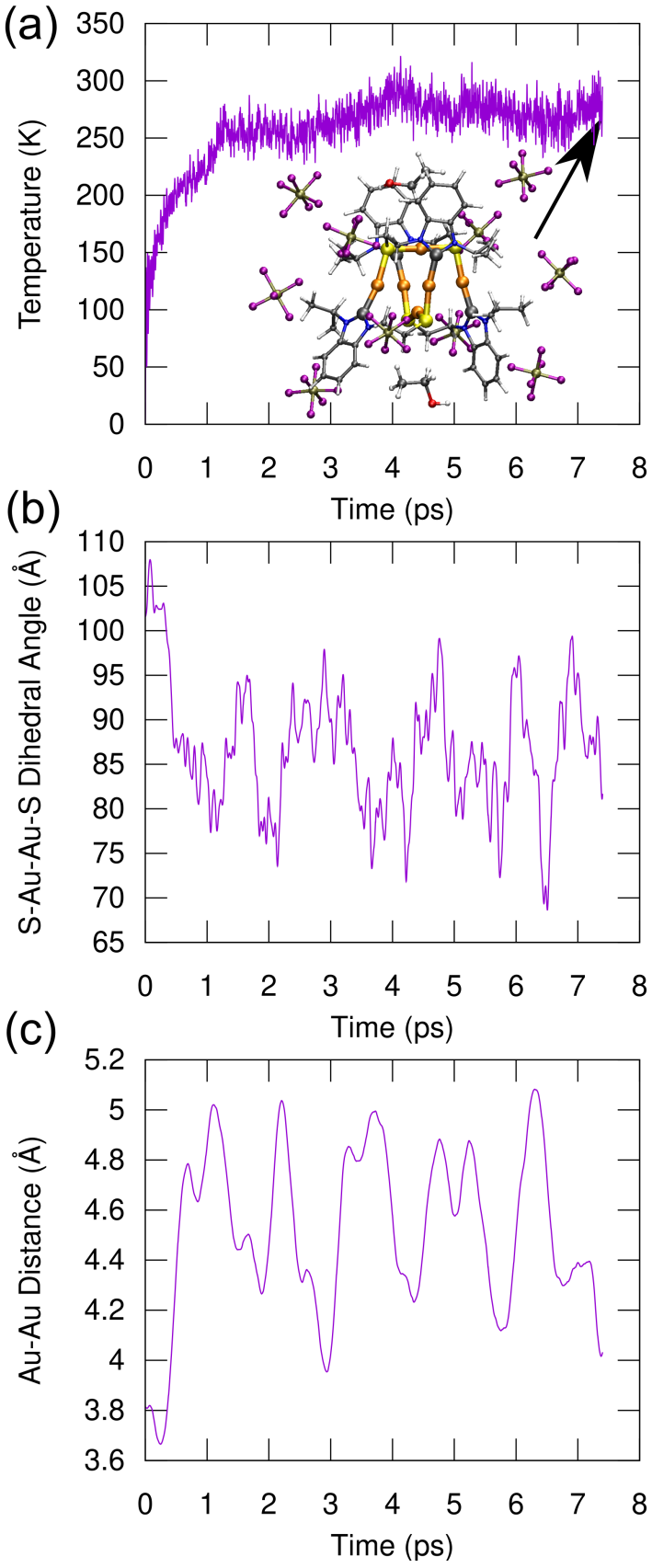

Fig. S8 Behavior of a) temperature, b) S-Au-Au-S dihedral angle, and c) Au-Au distance as a function of time during MD-simulation at 269K (average after thermalization) for the most stable gas phase Au_6 cluster isomer surrounded by 10 PF_6^- counterions and 2 EtOH molecules fixed to symmetry and positions found from crystal structure. Inset figure in panel a) shows the last frame structure of the MD-run.