Supporting Information

S-TABLE 1. Partial molecular orbital contributions (%) of the lowest-energy $^3A''$ excited state of $[Au_2(PH_2CH_2PH_2)(SHCH_2SH)]^{2+}\cdot(MeCN)_2$ (**2**·$(MeCN)_2$) under the CIS calculations.

Oribal	Bond	Energy	Contribution (%)				Au Components			Others Components
		(eV)	2Au	2P	2S	2N	s	p	d	
39a′	π+π(P_2)	–2.081	31	34	1	1		22% p_x 5% p_z		25% p_x (P) 6% p_z(P)
31a″	π*	–2.311	87	5	5	0		86% p_y		
38a′	σ	–2.699	64	6	4	1	14% s	47% p_z		
30a″	π*	–3.041	88	3	0	0		77% p_x 7% p_z		
37a′	π	–3.136	45	18	10	0		42% p_y		8% s (P) 8% p_z(P) 6% s(S) 3% p_x(S)
29a″	σ*	–3.216	64	8	3	2		7% p_x 51% p_z		8% s(P)
36a′	π	–4.648	61	7	1	0		58% p_x		
35a′	σ	–6.189	52	24	14	3	31% s	11% p_z	5% d_{x2}	11% s(P) 12% p_y(P) 12% p_y(S)
HOMO–LUMO Gap										
28a″	σ*	–14.697	53	21	15	7			38% d_{y2-z2} 11% d_{x2}	7% s(P) 14% p_y(P) 10% p_y(S)
27a″	L(S)	–16.203	9	10	77	1				7% p_y(P) 28% p_y(S) 46% p_z(S)
34a′	L(S)	–16.692	8	4	74	2				68% p_y(S)
33a′	σ+σ*(Au–P)	–17.199	48	26	1	8	12% s	6% p_z	24% d_{x2}	23% p_y(P)
26a″	σ*	–18.103	80	3	8	3			21% d_{y2-z2} 55% d_{yz}	
25a″	π*+π(C≡N)	–18.164	79	0	0	11			78% d_{xz}	10% p_x(N)
24a″	σ*	–18.308	77	4	1	9			22% d_{y2-z2} 24% d_{yz} 25%	6% p_y(N)
23a″	σ*+L(S)+π(C≡N)	–18.676	36	1	31	12			7% d_{y2-z2} 25% d_{x2}	6% s(S) 12% p_y(S) 9% p_z(S) 12%
32a′	π+π(C≡N)	–18.846	21	0	0	40			19% d_{xz}	39% p_x(N)
31a′	π+π(C≡N)	–18.887	21	0	3	38			16% d_{yz}	35% p_y(N)
22a″	δ*	–19.141	94	1	0	2			91% d_{xy}	
30a′	δ	–19.303	83	2	6	2			80% d_{xy}	31% p_x(N)
21a″	π*+π(C≡N)	–19.391	37	0	0	32			34% d_{xz}	31% p_x(N)
29a′	σ	–19.399	81	1	1	11			35% d_{y2-z2} 38% d_{x2}	6% s(N)
20a″	π*+π(C≡N)	–19.602	24	13	14	17			17% d_{yz}	6% p_y(S) 16% p_y(N)
28a′	σ+L(S)	–19.681	37	2	37	3			10% d_{y2-z2} 9% d_{yz} 15% d_{xy}	13% s(S) 15% p_x(S) 8% p_z(S)
19a″	π*+ L(P)	–20.005	26	31	1	6			22% d_{yz}	26% p_z(P) 5% p_y(N)
27a′	π	–20.221	89	0	0	5			88% d_{xz}	5% p_x(N)
26a′	π	–20.278	81	2	3	5			72% d_{yz} 7% d_{x2}	
25a′	σ	–20.418	58	7	8	5			24% d_{y2-z2} 29% d_{x2}	
18a″	σ(Au–P/S)	–20.515	69	15	11	0			13% d_{y2-z2}	11% p_y(P) 8% p_y(S)

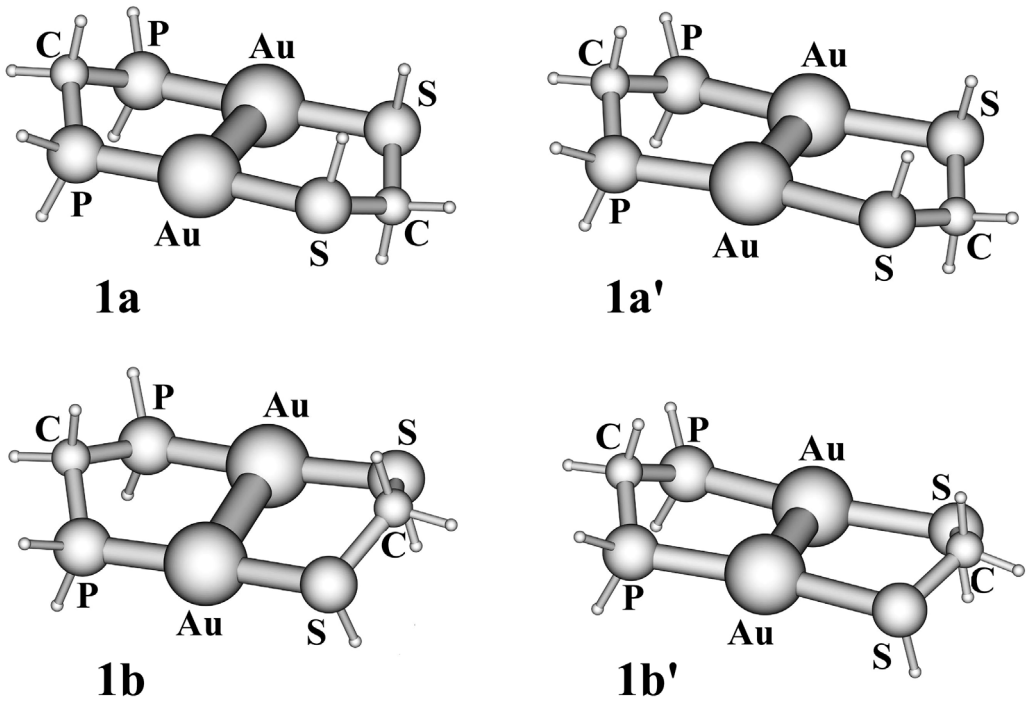
S-TABLE 2. Partial molecular orbital contributions (%) of the lowest-energy ^3A_u excited state of $[Au_2(SHCH_2SH)_2]^{2+}\cdot(MeCN)_2$ (**3**$\cdot(MeCN)_2$) under the CIS calculations.

Orbital	Bond	Energy	Contribution (%)			Au Components			Others Components	
		(eV)	2Au	4S	2N	s	p	d		
$35a_u$	L(S)	–2.129	8	43	0		7% p_y		7% s(S)	11% p_z(S)
$35a_g$	π*	–2.413	86	12	0		85% p_y		5% s(S)	
$34a_g$	σ	–2.985	55	12	0	11% s	44% p_z			
$33a_g$	π*	–3.110	93	2	0		90% p_x			
$34a_u$	σ*	–3.328	59	11	2		54% p_z		6% s(S)	
$33a_u$	π	–3.366	48	27	0		45% p_y		6% s(S)	6% p_x(S)
$32a_u$	π	–4.667	69	4	0		68% p_x			
$32a_g$	σ	–6.715	56	35	4	34% s	12% p_z	6% d_{x2}		15% p_y(S)
HOMO–LUMO Gap										
$31a_u$	σ*	–15.165	50	43	5			37% d_{y2-z2} 10% d_{x2}	15% p_y(S)	6% p_z(S)
$31a_g$	L(S)	–16.697	3	96	0				19% p_y(S)	28% p_z(S)
$30a_u$	L(S)+σ(Au–S)	–17.238	8	79	1				36% p_y(S)	
$30a_g$	σ+σ(Au–S)	–17.381	40	41	7	9% s	7% p_z	21% d_{x2}	19% p_y(S)	
$29a_u$	σ*	–17.746	41	48	4			37% d_{y2-z2}		18% p_z(S)
$29a_g$	π*	–18.337	80	4	7			76% d_{yz}		6% p_y(N)
$28a_g$	π*	–18.369	76	0	12			72% d_{xz}		11% p_x(N)
$28a_u$	σ*	–18.857	86	11	0			18% d_{y2-z2} 61% d_{x2}		
$27a_u$	π	–19.036	17	0	42			17% d_{xz}		40% p_x(N)
$27a_g$	L(S)+π(C≡N)	–19.087	6	30	29				7% p_y(S)	29% p_y(N)
$26a_u$	π+π(C≡N)	–19.099	15	2	42			14% d_{yz}		40% p_y(N)
$26a_g$	δ	–19.415	75	18	1			8% d_{x2} 65% d_{xy}		
$25a_u$	δ*	–19.422	98	1	0			95% d_{xy}		
$25a_g$	π*+π(C≡N)	–19.626	41	0	30			41% d_{xz}	30% p_x(N)	
$24a_g$	σ	–19.686	81	1	13			40% d_{y2-z2} 34% d_{x2}	7% s(N)	
$24a_u$	π+L(S)	–20.076	45	35	1			44% d_{yz}	6% s(S) 6% p_x(S)	5% p_z(S)
$23a_g$	σ+L(S)	–20.102	68	23	4			10% d_{y2-z2} 19% d_{x2} 38% d_{xy}		
$22a_g$	π+σ(Au–S)	–20.306	34	35	10			32% d_{yz}	8% p_y(S) 5% p_z(S)	10% p_y(N)
$23a_u$	π	–20.585	91	0	4			90% d_{xz}		
$22a_u$	π+L(S)	–20.804	51	21	3			50% d_{yz}	7% p_x(S)	
$21a_g$	σ+σ(Au–S)	–20.940	44	25	3			15% d_{y2-z2} 23% d_{x2}		
$21a_u$	σ(Au–S)	–21.013	55	36	0			12% d_{y2-z2} 41% d_{x2}	14% p_y(S)	

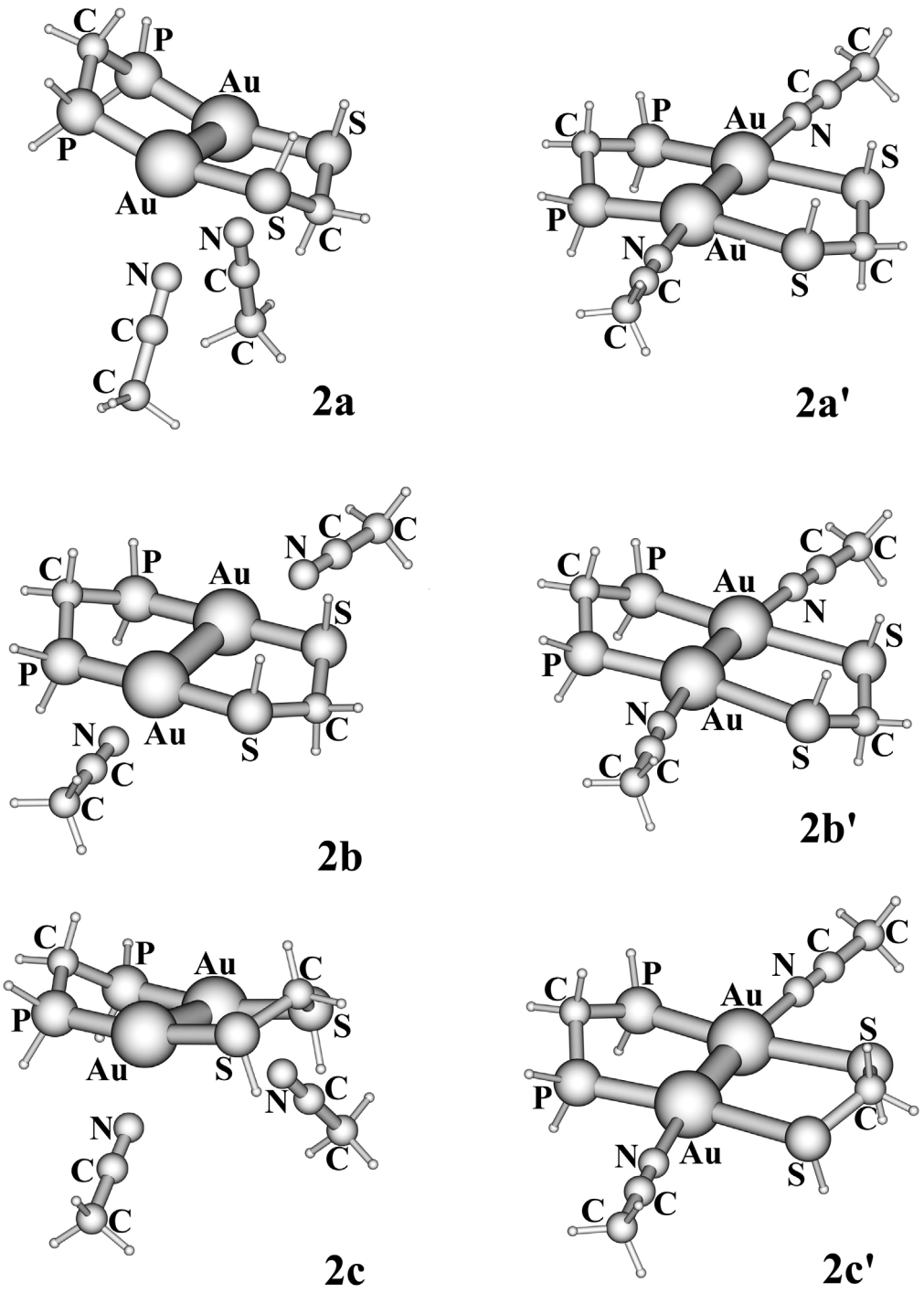
S-TABLE 3. The optimized geometry parameters of $[Au_2(PH_2CH_2PH_2)(SCH_2S)]$ (**6**) head-to-tail $[Au_2(PH_2CH_2SH)_2]^{2+}$ (**7**), head-to-head $[Au_2(PH_2CH_2SH)_2]^{2+}$ (**8**), head-to-tail $[Au_2(PH_2CH_2SH)_2]^{2+}\cdot(MeCN)_2$ (**7**·$(MeCN)_2$), and head-to-head $[Au_2(PH_2CH_2SH)_2]^{2+}\cdot(MeCN)_2$ (**8**·$(MeCN)_2$) using the MP2 method for the ground state and the CIS method for the excited state.*

Parameters	**6**		**7**		**8**		**7**·$(MeCN)_2$		**8**·$(MeCN)_2$	
	$^1A'$	$^3A''$	^1A_g	^3A_u	^1A	^3A	^1A_g	^3A_u	^1A	^3A
Au–Au	3.011	2.879	2.979	2.715	2.972	2.994	2.953	2.657	2.996	2.730
Au–P	2.318	2.487	2.341	2.558	2.372	2.435	2.318	2.623	2.370	2.556
Au–S	2.336	2.457	2.424	2.705	2.396	2.894	2.449	2.981	2.427	2.892
P–C	1.877	1.873	1.875	1.861	1.875	1.859	1.873	1.854	1.874	1.856
S–C	1.867	1.832	1.865	1.842	1.866	1.834	1.860	1.835	1.860	1.834
Au–N							2.567	2.336	2.587	2.441
P···P	3.062	3.189								
S···S	3.200	2.890								
P···S			3.160	3.154	3.160	3.129	3.132	3.078	3.124	3.091
P–Au–S	176.4	171.4	174.9	170.1			167.9	169.8		
P–Au–P					175.9	178.8			166.0	176.6
S–Au–S					168.7	178.5			170.9	171.2
P–Au–Au	90.6	93.6	87.1	94.5	88.0	90.6	89.0	94.8	83.0	91.7
S–Au–Au	92.3	90.1	97.0	94.9	95.7	90.7	94.2	93.1	94.5	94.4
N–Au–Au							104.0	174.3	180.0	180.0
P/S–Au–Au–S/P	177.9	172.2	177.0	177.0	168.5	169.4	168.4	173.6	151.9	168.8
Emiss. Ener. (eV / nm)	2.68 / 462		3.68 / 337		3.24 / 383		2.02 / 614		2.62 / 473	

*The calculated results of **6** have been published in ref. 55, and those of **7** and **8** in ref. 54.



S-Figure 1. The optimized $^{1}A'$ ground-state structures by the MP2 method for **a**. chair conformation, and **b**. boat conformation, as well as the optimized $^{3}A''$ excited-state structures by the CIS method for **a′**. chair conformation, and **b′**. boat conformation of $[Au_2(PH_2CH_2PH_2)(SHCH_2SH)]^{2+}$ (**2**).



S-Figure 2. The optimized ground-state structures by the MP2 method for **a**. chair conformation (^{1}A′), **b**. chair conformation, and **c.** boat conformation (^{1}A′), as well as the optimized excited-state structures by the CIS method for **a′**. chair conformation (^{3}A″), **b′**. chair conformation, and **c′**. boat conformation (^{3}A″) of $[Au_2(PH_2CH_2PH_2)(SHCH_2SH)]^{2+}\cdot(MeCN)_2$ (**2**·$(MeCN)_2$).