Supporting Information for

Near-white light emission from single crystals of cationic dinuclear gold(I) complexes with bridged diphosphine ligands

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Contents

1. General Information

^{1}H and ^{31}P NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. ^{1}H chemical shifts were referenced to residual solvent peaks. ^{31}P chemical shifts were referenced to an external standard, 85% phosphoric acid (δ = 0 ppm). Elemental analyses (C and H) were carried out using an elemental analyser (Vario EL CHNOS) from Elementar. For the photo-physical studies, dissolved oxygen was removed by repeated freeze-pump-thaw cycles. Steady-state emission spectra were recorded at room temperature and at 77 K using a Hitachi F-7000 spectrofluorometer. The intensity distribution of the Xenon lamp incorporated in the spectrofluorometer was corrected using Rhodamine B in ethylene glycol. The output of the photomultiplier tube was calibrated between 300 and 850 nm with a secondary standard lamp.

Laser photolysis studies were performed using a Nd:YAG laser (Minilite II, Continuum Ltd.) equipped with second, third, and fourth harmonic generators. The laser pulses used for the emission lifetime measurements were of the third harmonic (355 nm). The duration and energy of the laser pulse were 5 ns and 8 mJ/pulse, respectively. The system used to monitor the emission decay was reported elsewhere.[S1]

An Optistat DN-V2 cryostat from Oxford Instruments was used to measure the emission spectra and lifetimes in the temperature range 293–83 K. Crystalline powders of samples used for emission measurements were sealed in quartz tubes with a diameter of 3 mm. Optical measurements at 77 K were carried out at the temperature of liquid nitrogen using a Dewar vessel with four optical windows. After filling the vessel with liquid nitrogen, the sample, which was placed in a quartz tube with a diameter of 5 mm, was immersed into the liquid nitrogen for rapid cooling, and luminescence spectra and lifetimes were measured.

Emission quantum yields were determined at room temperature and at 77 K using an absolute PL quantum yield measurement system (C-9920-02G, Hamamatsu).[S2]

A suitable crystal for **1**, **2**, and **3** was selected and mounted using Paratone-N oil on a Cryo-Loop. X-ray Diffraction data was collected at 93 K under a cold nitrogen gas stream on a Rigaku XtaLAB Pro MM007HF Synergy-DW X-ray diffractometer system, using graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å). Intensity data were collected by an ω-scan with 0.5° oscillations for each frame. Bragg spots were integrated using the CrysAlis^{Pro} program package.[S3] Structures were solved by SHELXT[S4] and refined by SHELXL.[S5] All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined by applying riding models. CCDC reference numbers are 2173250 for **1**, 2173251 for **2**, and 2173252 for **3**, respectively.

The PBE[S6]-D3(BJ)[S7]/TZP[S8] level of theory was applied for all density functional theory (DFT)

calculations using the ADF2019.303 package.[S9,S10] All calculations were performed with tight criteria (very good).

The ground state (S_0), first excited singlet state (S_1), the first excited triplet state (T_1) and the second triplet state (T_2) were optimized by TD-DFT calculations at gas-phase conditions.[S11] The input coordinates were extracted from the X-ray crystallographic data at 93 K. The perturbative spin-orbit coupling (p-SOC) calculations[S10f] for the first 50 singlet and triplet excited states were performed at the same level of theory. Natural transition orbitals (NTOs) were generated by orbital transformation followed by a singular value decomposition of the transition density matrix. In the NTO representation, the electronic transitions can be expressed by one single "hole (approximately HOMO) - electron (approximately LUMO)" pair with an associated eigenvalue of essentially one, even for transitions that are highly mixed in the canonical MO basis. This procedure can be a helpful strategy for obtaining a simple orbital interpretation of "what got excited to where".[S12]

2. NMR Experiments

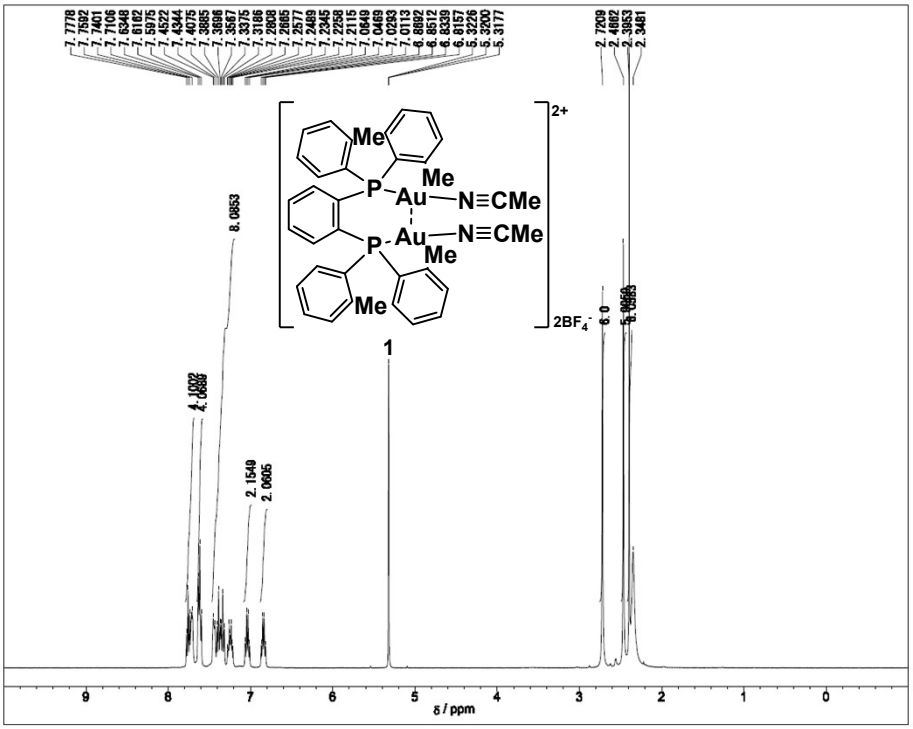


Fig. S1 ^{1}H NMR spectrum of **1** in CD_2Cl_2 at 293 K.

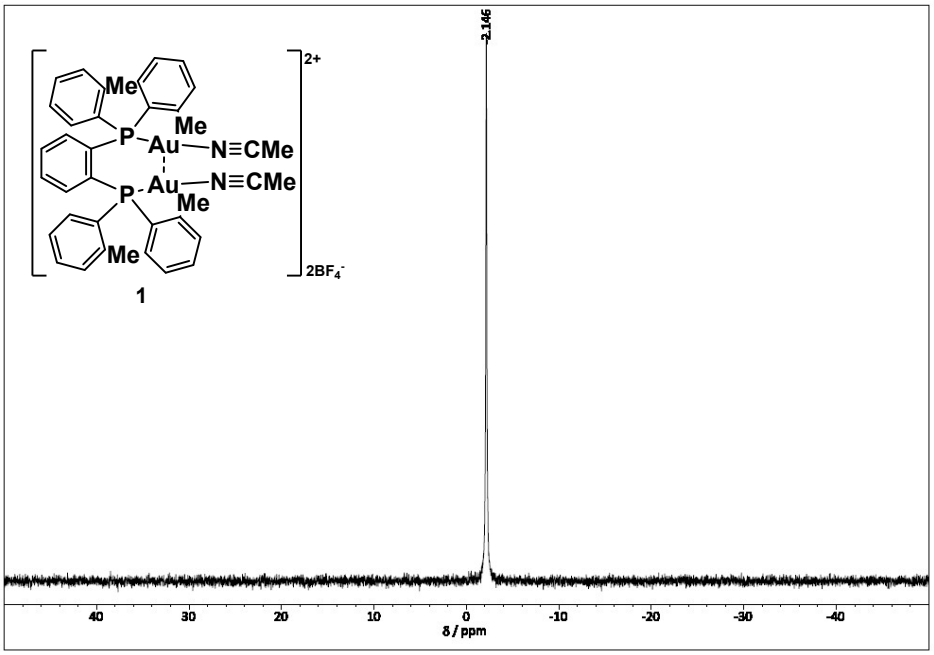


Fig. S2 ^{31}P $\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2 at 293 K.

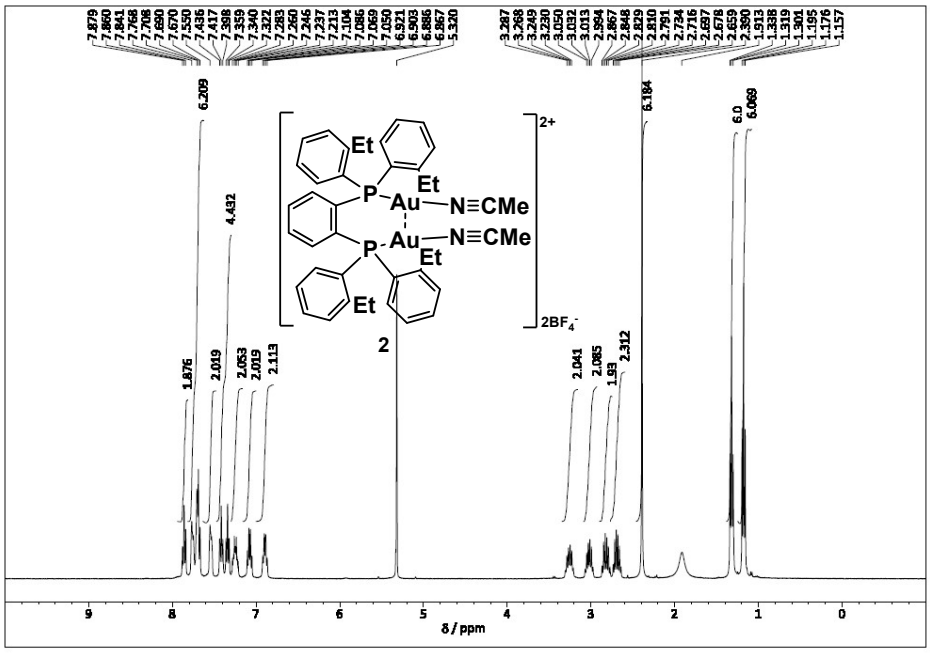


Fig. S3 ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 293 K.

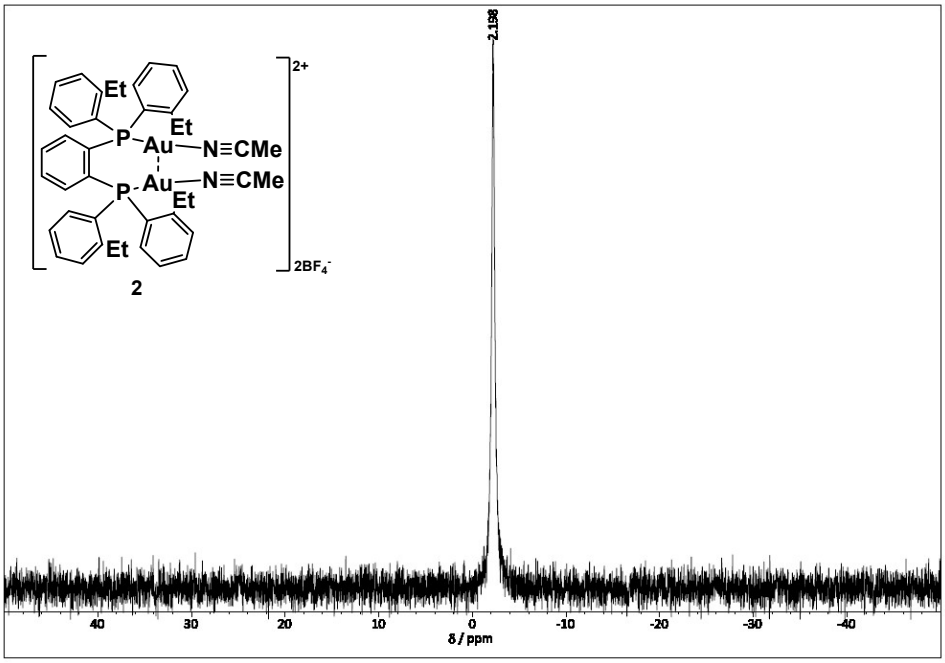


Fig. S4 ^{31}P $\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2 at 293 K.

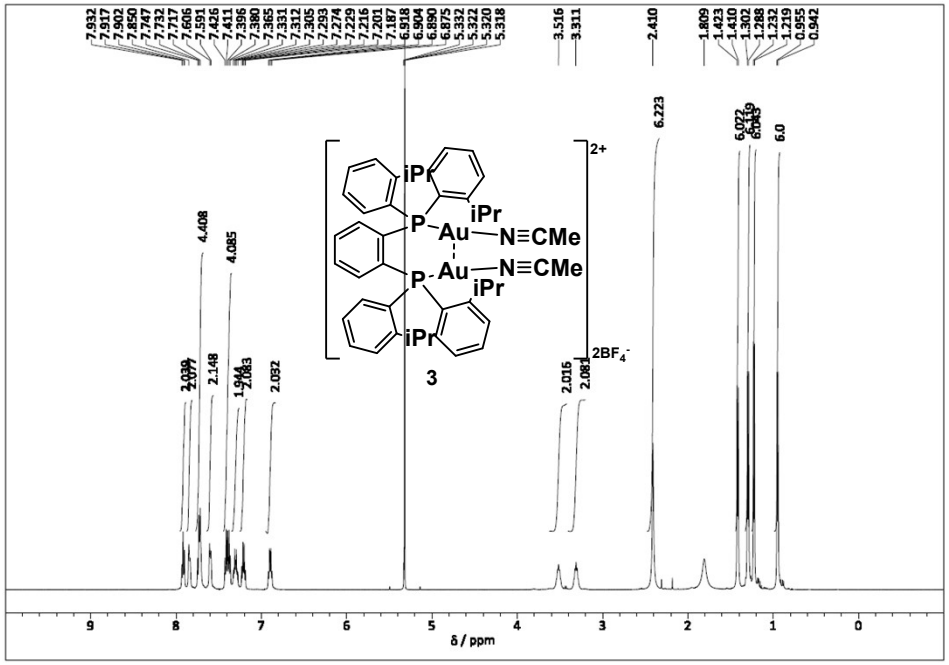


Fig. S5 ^{1}H NMR spectrum of **3** in CD_2Cl_2 at 293 K.

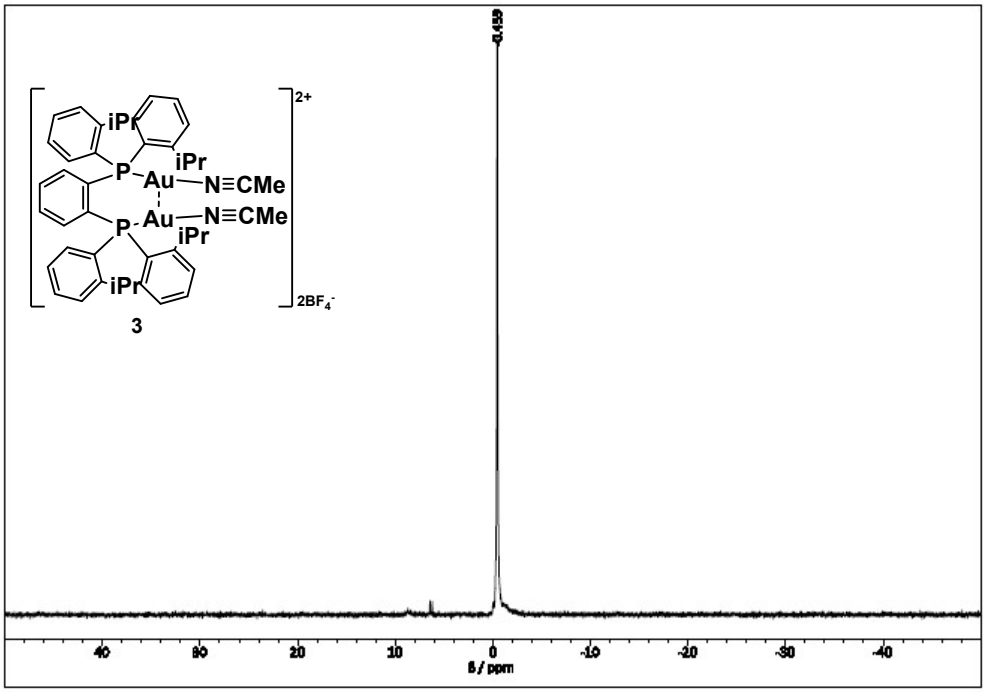


Fig. S6 ^{31}P $\{^{1}H\}$ NMR spectrum of **3** in CD_2Cl_2 at 293 K.

3. Crystal Structure determination

Table S1. Crystallographic data for **1**•$2CH_2Cl_2$, **2** and **3**

	1•$2CH_2Cl_2$	**2**	**3**•$2H_2O$
formula	$C_{38}H_{38}Au_2N_2P_2$• $2(CH_2Cl_2)$ •$2(BF_4)$	$C_{42}H_{46}Au_2N_2P_2$•$2(BF_4)$	$C_{46}H_{54}Au_2N_2P_2$•$2(BF_4)$ •$2H_2O$
formula weight	1322.05	1208.30	1282.42
cryst syst	triclinic	orthorhombic	orthorhombic
space group	*P*	*Fdd*2	*Fdd*2
a / Å	11.87700(18)	26.9142(12)	28.1116(8)
b / Å	12.1739(2)	24.8726(17)	23.6525(7)
c / Å	16.1311(4)	13.0916(6)	14.2329(5)
α / deg	96.5705(16)	90	90
β / deg	98.6092(15)	90	90
γ / deg	99.5936(13)	90	90
V / Å^3	2250.50(7)	8763.9(8)	9463.6(5)
Z	2	8	8
d_{calcd} / g cm^{-3}	1.951	1.832	1.800
T / K	93(2)	93(2)	93(2)
radiation	Cu Kα ((λ = 1.54184 Å)	Cu Kα (λ = 1.54184 Å)	Cu Kα (λ = 1.54184 Å)
μ / cm^{-1}	15.513	13.672	12.718
diffractometer	Rigaku XtaLAB Pro MM007HF	Rigaku XtaLAB Pro MM007HF	Rigaku XtaLAB Pro MM007HF
max 2θ / deg	75	75	75
reflns collcd	42133	10347	12087
indep reflns	9088 (*R*int = 0.0554)	4461 (*R*int = 0.0572)	4860 (*R*int = 0.0268)
no. of param refined	547	265	294
R1,[a] *wR2* ($I > 2\sigma I$)[b]	0.0448, 0.1078	0.0611, 0.1673	0.0239, 0.0616
S	1.090	1.053	1.073

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

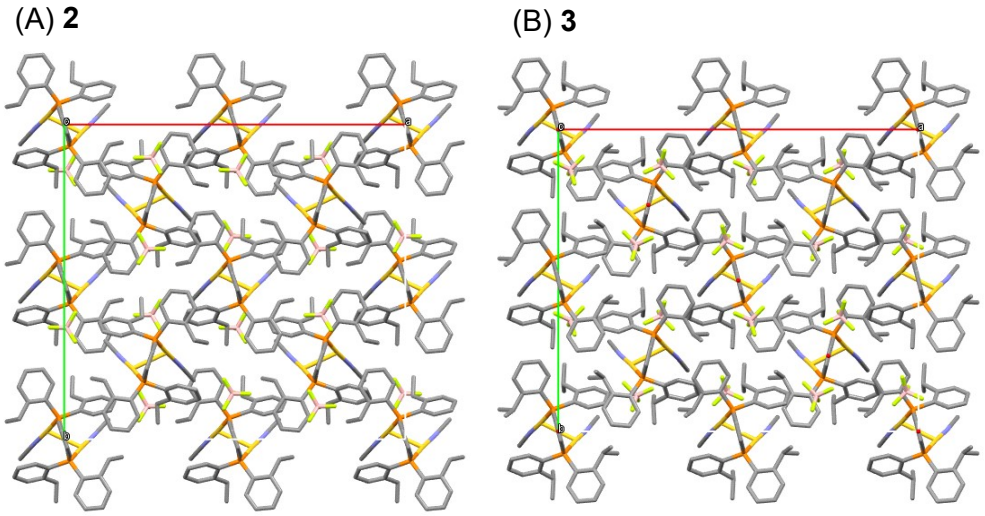


Fig. S7 Packing structuress of **2** (A) and **3** (B); view along c axis.

4. Photophysical Properties

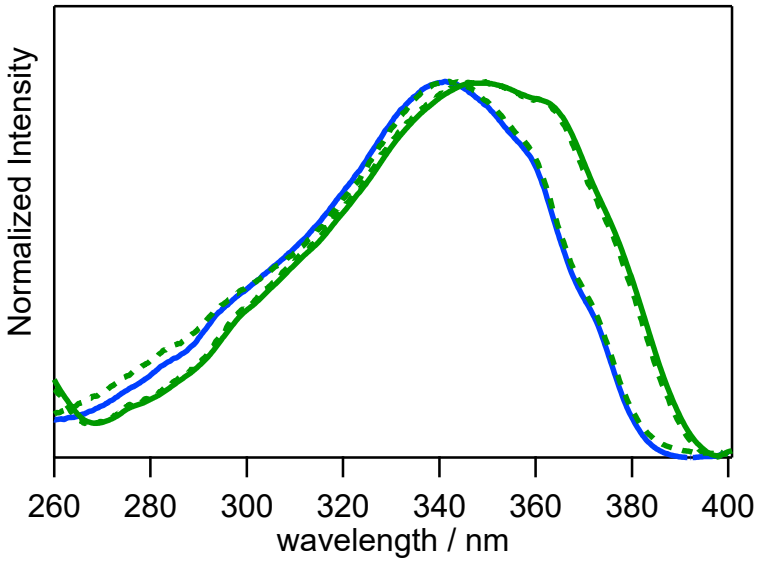


Fig. S8 Excitation spectra of **1** and **2**: the monitoring wavelength at λ_{em} = 415 nm (blue solid line) and 600 nm (blue dashed) for **1**, and 430 nm (green solid) and 630 nm (green solid) for **2** at 293 K .

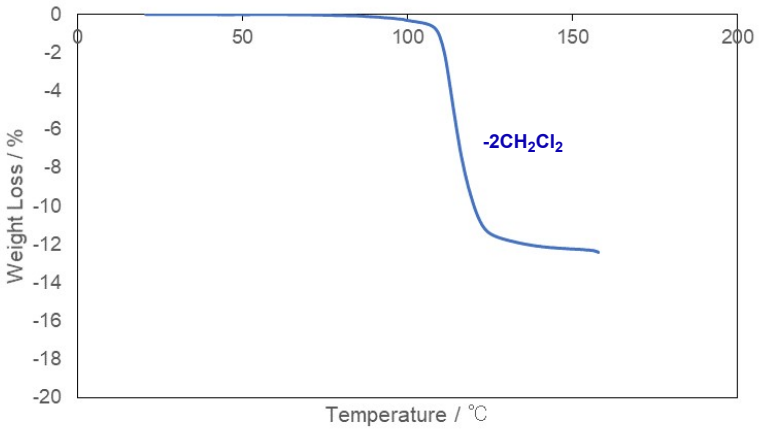


Fig. S10 TGA data for **1**•$2C_2Cl_2$ under argon atmosphere with a heating rate of 20℃ min^{-1}.

Table S2. Temperature-dependent changes of lifetimes

(A) Complex **2**

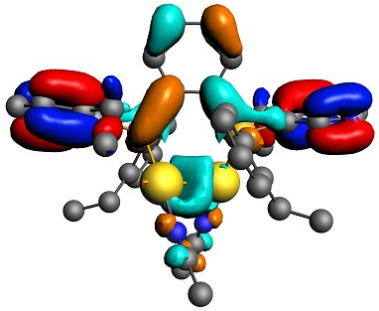
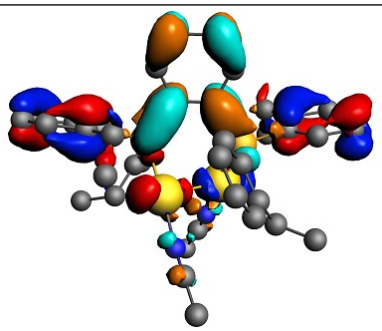
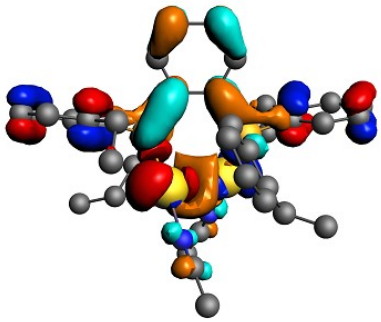
Temp. / K	τ / μs at 430 nm	τ / μs at 600 nm
293.0	3.9	3.8
273.6	7.5	7.4
254.2	13.0	12.8
234.9	18.4	18.0
215.5	23.0	23.0
196.1	26.0	26.0
176.7	24.0	24.0
157.3	23.7	23.5
138.0	23.4	-
118.6	23.8	-
99.2	24.1	-
83.9	24.4	-
77.0	26.2	-

(B) Complex **3**

Temp. / K	τ / μs at 430 nm	τ / μs at 500 nm	τ / μs at 590 nm
322.1	9.2	9.2	9.7
309.5	10.6	10.7	11.4
293.0	12.8	12.8	13.0
263.9	17.9	17.7	17.9
234.9	25.1	24.8	25.0
205.8	33.6	33.4	33.7
176.7	41.9	42.4	41.0
147.6	49.1	49.1	44.6
118.6	52.2	53.7	-
108.9	52.7	55.1	-
99.2	53.2	55.3	-
94.3	53.4	55.3	-
89.5	53.4	55.2	-
83.8	53.5	55.2	-
77.0	53.5	55.3	-

Table S3 Natural transition orbital (NTO) analyses (A) for **2** and (B) for **3** at the structure determined by X-ray crystallography

(A) Complex **2**

	λ_{cal} / eV (nm)	*f*	NTO pairs Isovalue = 0.035 Hole (red and blue) Electron (cyan and orange)	Generation probability (%)	Main Character
T_2	3.296 (376)	0.0002		99.8	ILCT (LMMCT, LL'CT)
S_1	3.226 (384)	0.0220		99.0	ILCT (MC, MLCT)
T_1	3.116 (398)	0.0005		99.8	ILCT (MC, MLCT)

(B) Complex **3**

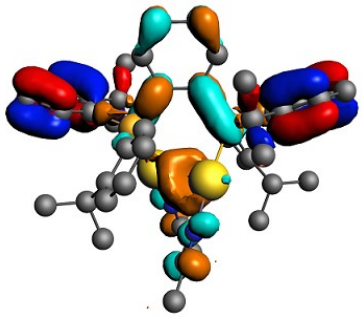
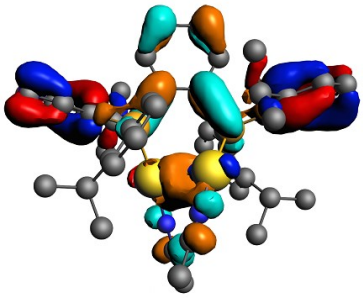
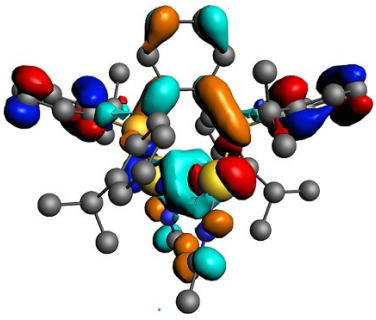
	λ_{cal} / eV (nm)	*f*	NTO pairs Isovalue = 0.035 Hole (red and blue) Electron (cyan and orange)	Generation probability (%)	Main Character
T_2	3.194 (388)	0.0004		99.9	ILCT (LMMCT, LL'CT)
S_1	3.183 (390)	0.0132		99.2	ILCT (MC, MLCT)
T_1	3.105 (399)	0.0004		99.8	ILCT (MC, LL'CT, LMMCT)

Table S4 Calculated energy differences between the sublevels (M1, M2, and M3) of the T_1 and T_2 states at the crystal structures for **2** (A) and **3** (B).

(A) 2

T_1	E^a / eV	Singlet and triplet contribution / %
M1	3.10598	$T_1(97.6) + T_4(1.08)$
M2	3.10665	$T_1(98.0) + T_4(1.08)$
M3	3.10665	$T_1(98.2) + S_6(0.36)$

T_2	E^a / eV	Singlet and triplet contribution / %
M1	3.28868	$T_2(96.7) + S_2(1.04) + S_8(0.7)$
M2	3.28868	$T_2(97.5) + T_7(1.08) + T_3(0.4)$
M3	3.28891	$T_2(97.3) + S_1(0.52) + S_3(0.30)$

(B) 3

T_1	E^a / eV	Singlet and triplet contribution / %
M1	3.09282	$T_1(97.0) + T_4(1.42)$
M2	3.09378	$T_1(97.3) + T_4(1.42) + T_3(0.91)$
M3	3.09466	$T_1(97.6) + S_5(0.48) + S_3(0.22)$

T_2	E^a / eV	Singlet and triplet contribution / %
M1	3.18469	$T_1(96.1) + S_1(1.12)$
M2	3.18482	$T_1(94.5) + S_1(2.94) + T_3(0.91)$
M3	3.18491	$T_1(96.8) + S_6(1.05) + S_2(0.56)$

[a] Energy

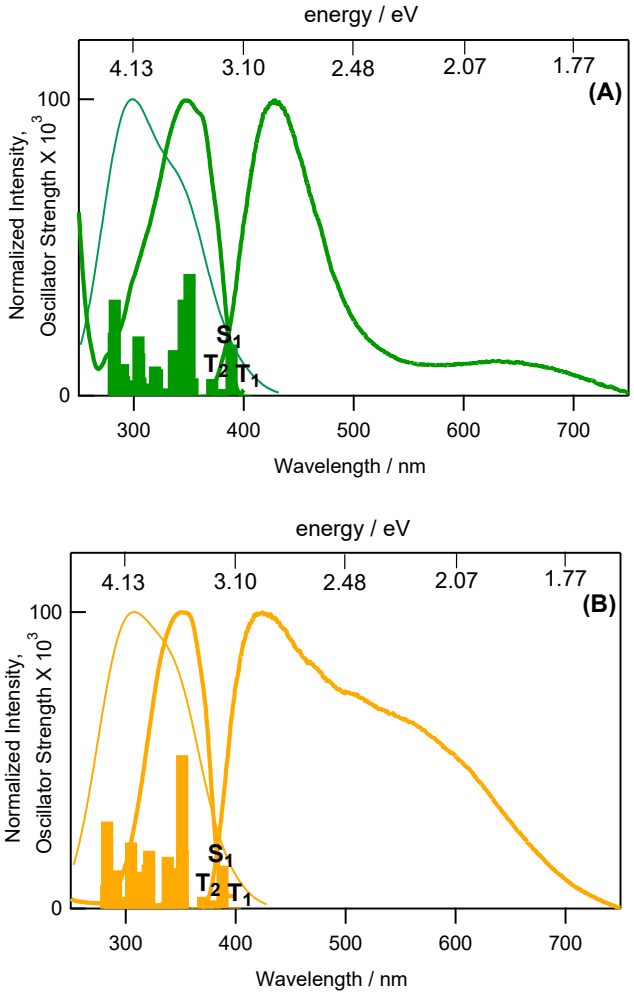
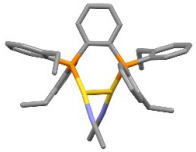


Fig. S10 Experimental corrected emission (right) and excitation spectra (left) at 293 K (bold line), and calculated absorption spectra (thin line) and FC singlet and triplet transitions (solid bar) at the optimized S_0 structures. (A) for **2** and (B) for **3**.

Table S5 Calculation results (A) for **2** and (B) for **3**: the optimized structures and excited state energy

(A)

The X-ray and the optimized structures of **2**	 Crystal structure	 **S_0**	 **S_1**	 **T_1**
Au–Au bond distance / Å	2.9841(8)	3.063	2.991	2.762
Total Bonding Energy / eV	-551.4314	-568.3279	-567.9912	-567.7228
Excited State Energy / eV	–	–	-565.3606	-565.6523
Excitation Energy / eV	–	–	2.6306	2.0706

(B)

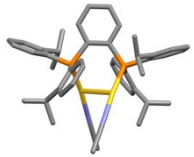
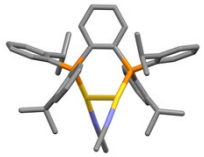
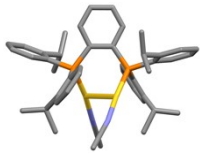
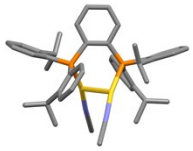
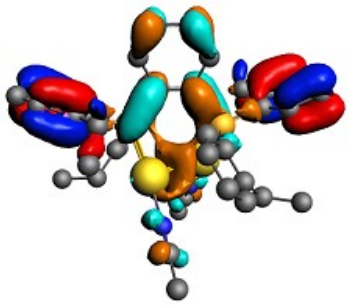
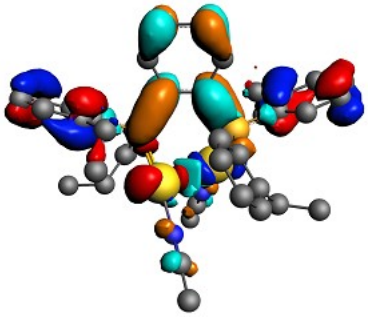
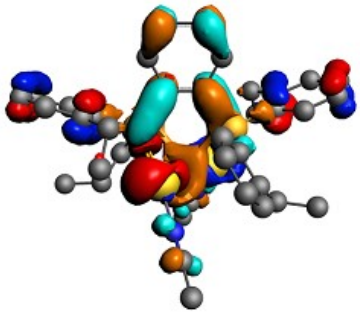
The X-ray and the optimized structures of **3**	 Crystal structure	 **S_0**	 **S_1**	 **T_1**
Au–Au bond distance / Å	3.0457(8)	3.101	3.043	2.782
Total Bonding Energy / eV	-616.4976	-634.8326	-634.3502	-634.2131
Excited State Energy / eV	–	–	-632.0046	-632.1523
Excitation Energy / eV	–	–	2.3457	2.0608

Table S6 Natural transition orbital (NTO) analyses (A) for **2** and (B) for **3** at the optimized S_0 structure

(A) Complex **2**

	λ_{cal} / eV (nm)	*f*	NTO pairs Isovalue = 0.035 Hole (red and blue) Electron (cyan and orange)	Generation probability (%)	Main Character
T_2	3.262 (380)	0.0002		99.8	ILCT (LMMCT, LL'CT)
S_1	3.197 (388)	0.0174		99.7	ILCT (MC, MLCT)
T_1	3.093 (401)	0.0003		99.7	ILCT (MC, MLCT)

(B) Complex **3**

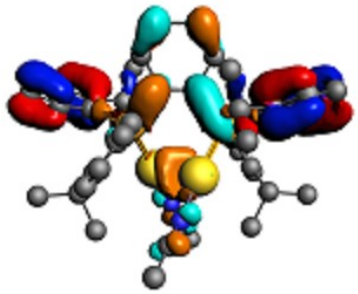
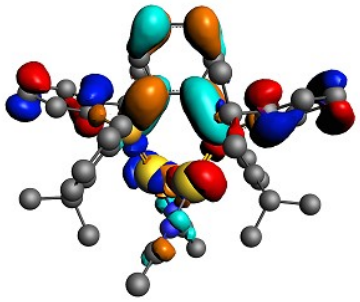
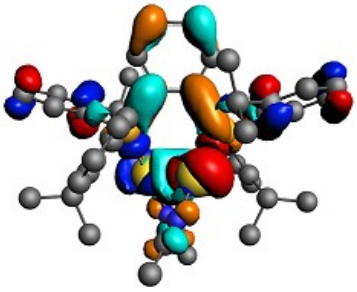
	λ_{cal} / eV (nm)	*f*	NTO pairs Isovalue = 0.035 Hole (red and blue) Electron (cyan and orange)	Generation probability (%)	Main Character
T_2	3.255 (381)	0.0002		99.8	ILCT (LMMCT, LL'CT)
S_1	3.203 (387)	0.0145		99.4	ILCT (MC, MLCT)
T_1	3.114 (398)	0.0003		99.7	ILCT (MC, LL'CT, LMMCT)

Table S7 Calculated energy differences between the sublevels (M1, M2, and M3) of the S_0 states for **2** (A) and **3** (B).

(A) 2

S_0 at T_1 structure	E^a / eV	Singlet and triplet contribution / %
M1	3.084100	T_1(99.6)
M2	3.084800	T_1(99.6)
M3	3.085490	T_1(98.5) + S_5(0.24)

S_0 at T_2 structure	E^a / eV	Singlet and triplet contribution / %
M1	3.255870	T_2(98.0)
M2	3.255950	T_2(97.7) + S_8(0.4) + S_2(0.2)
M3	3.255990	T_2(97.7) + S_1(0.6) + S_3(0.3)

(B) 3

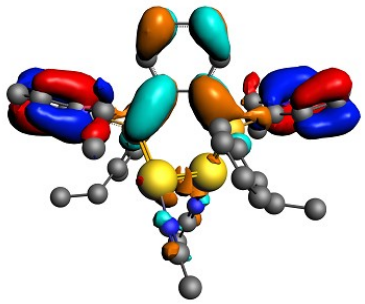
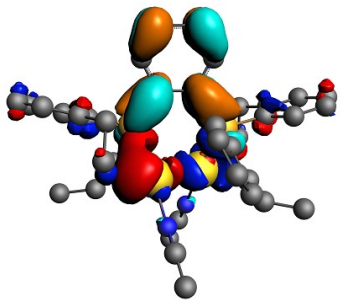
S_0 at T_1 structure	E^a / eV	Singlet and triplet contribution / %
M1	3.105290	T_1(98.4)
M2	3.106050	T_1(97.4))
M3	3.106570	T_1(98.4) + S_5(0.25)

S_0 at T_2 structure	E^a / eV	Singlet and triplet contribution / %
M1	3.249610	T_1(99.6)
M2	3.249710	T_1(99.7))
M3	3.249790	T_1(97.3) + S_1(1.0)

[a] Energy

Table S8 Natural transition orbital (NTO) analyses (A) for **2** and (B) for **3** at the optimized S_1 and T_1 structures.

(A) Complex **2**

	λ_{cal} / eV (nm)	*f*	NTO pairs Isovalue = 0.035 Hole (red and blue) Electron (cyan and orange)	Generation probability (%)	Main Character
S_1	2.598 (477)	0.0036		97.7	ILCT
T_1	2.071 (599)	0.0001		99.9	MLCT

(B) Complex **3**

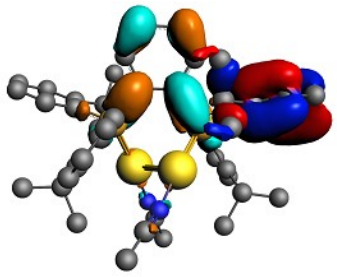
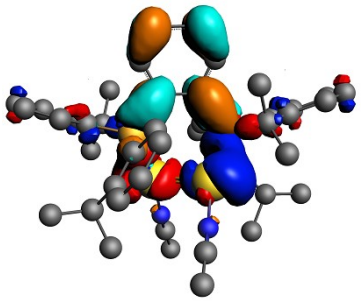
	λ_{cal} / eV (nm)	*f*	NTO pairs Isovalue = 0.035 Hole (red and blue) Electron (cyan and orange)	Generation probability (%)	Main Character
S_1	2.346 (528)	0.0010		99.8	ILCT
T_1	2.061 (602)	0.0001		99.9	MLCT

Table S9 Calculated energy differences between the sublevels (M1, M2, and M3) of the T_1 states for **2** (A) and **3** (B).

(A) complex 2

T_1 at T_1 structure	E^a / eV	Singlet and triplet contribution / %
M1	2.06640	T_1(99.6)
M2	2.06650	T_1(99.6)
M3	2.06666	T_1(99.6) + S_6(0.36)

(B) complex 3

T_1 at T_1 structure	E^a / eV	Singlet and triplet contribution / %
M1	2.05644	T_1(99.6)
M2	2.05656	T_1(99.6))
M3	2.05698	T_1(99.6) + S_{11}(0.1)

[a] Energy

Table S10 Calculated energy levels, emission energy, and oscillator strength valued of the S_0, S_1, and T_1 at each optimized structure for **2** (A) and **3** (B)

(A)

Structure	Excited state	Energy / eV	Emission energy / eV (nm)	Oscillator strength, *f*
Optimized $\mathbf{T_1}$	T_2	-564.9918	2.7310 (454)	0.0001
	S_1	-565.5555	2.1673 (572)	0.0082
	T_1	**-565.6522**	**2.0706 (599)**	**0.0001**
	S_0	-567.7228	-	-
Optimized $\mathbf{S_1}$	T_2	-565.2229	2.7683 (474)	0.0001
	S_1	**-565.3928**	**2.5984 (477)**	**0.0036**
	T_1	-565.4291	2.5621 (484)	0.0000
	S_0	-567.9912	-	-
Optimized $\mathbf{S_0}$	T_2	-565.0656	3.2619 (380)	0.0001
	S_1	-565.1024	3.1971 (388)	0.0220
	T_1	-565.2345	3.0934 (401)	0.0005
	S_0	**-568.3279**	-	-

(B)

Structure	Excited state	Energy / eV	Emission energy / eV (nm)	Oscillator strength, *f*
Optimized $\mathbf{T_1}$	T_2	-631.5021	2.7110 (457)	0.0000
	S_1	-632.0606	2.1525 (576)	0.0091
	T_1	**-632.1523**	**2.0608 (602)**	**0.0001**
	S_0	-634.2131	-	-
Optimized $\mathbf{S_1}$	T_2	-631.6769	2.6733 (464)	0.0001
	S_1	**-632.0045**	**2.3457 (529)**	**0.0036**
	T_1	-632.0196	2.3306 (532)	0.0000
	S_0	-634.3502	-	-
Optimized $\mathbf{S_0}$	T_2	-631.5772	3.2553 (381)	
	S_1	-631.6291	3.2034 (387)	
	T_1	-631.7182	3.1143 (398)	
	S_0	**-634.8326**	-	-

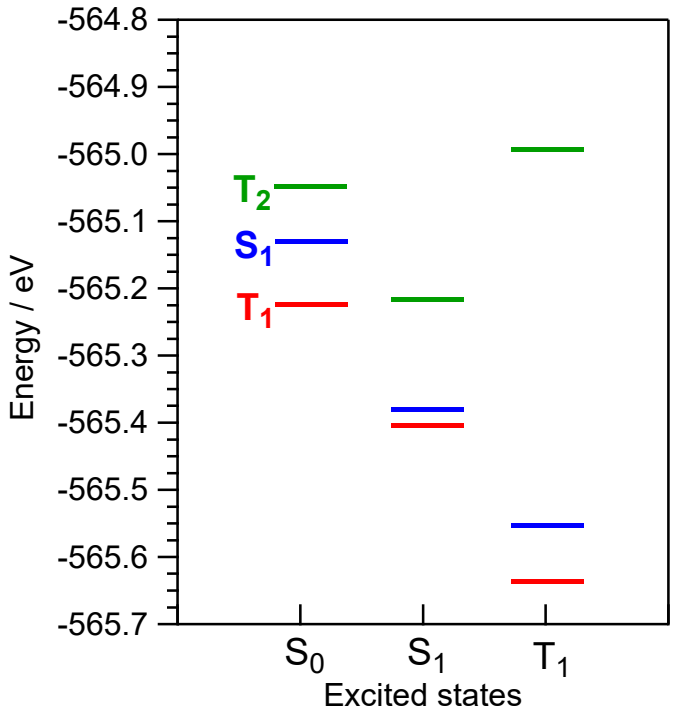


Fig. S11 Calculated energy levels of the S_1, T_1, and T_2 at each optimized structure for **2**

Table S11 Geometry data of **2** for the optimized S_1 state

Au	14.834527	13.021895	7.623011
P	13.879044	14.146937	5.872142
C	13.763516	13.791180	3.158951
H	13.992920	14.855709	3.134768
C	11.143129	14.523456	5.627390
H	11.287912	13.929158	4.723951
C	13.635538	13.143675	4.416278
N	15.969647	12.188400	9.139456
C	13.255802	16.039937	8.482061
H	14.196194	15.597117	8.122415
H	13.086144	15.596778	9.478161
C	9.703770	15.738721	7.128278
H	8.713278	16.103305	7.406794
C	12.107880	15.638305	7.581767
C	10.812774	16.069119	7.908366
H	10.676102	16.697869	8.791804
C	9.867498	14.960537	5.980893
H	9.010426	14.708148	5.354882
C	13.610151	13.127465	1.956066
H	13.725317	13.670540	1.018273
C	12.261903	14.850188	6.416013
C	16.211831	15.560822	4.976149
C	16.884403	16.751723	4.573413
H	17.944903	16.683301	4.322135
C	14.831377	15.637239	5.306352
C	17.012928	14.297035	5.015216
H	17.585727	14.225742	4.075701
H	16.357108	13.420019	5.060336
C	14.179775	16.862242	5.185224
H	13.113716	16.930362	5.402591
C	18.002617	14.279128	6.199235
H	18.586351	13.349904	6.175226
H	17.460820	14.325856	7.154126
H	18.701736	15.124402	6.158127
C	16.228075	17.969509	4.469765
H	16.764756	18.862346	4.147844
C	14.866072	18.029170	4.771113
H	14.320422	18.970165	4.687322
C	16.589900	11.632702	9.947278
C	17.365171	10.944707	10.953729
H	17.689195	9.9705278	10.561894
H	16.758423	10.78847	11.856807
H	18.251800	11.53917	11.215808
C	13.438115	17.555858	8.631370
H	13.658615	18.027194	7.663928
H	14.271283	17.776148	9.311575
H	12.539422	18.038302	9.037616
P	13.035156	10.725663	5.872142
C	13.150684	11.081420	3.158951
H	12.921280	10.016891	3.134768
C	15.771071	10.349144	5.627390
H	15.626288	10.943442	4.723951
C	13.278662	11.728925	4.416278
C	13.658399	8.832663	8.482061
H	12.718006	9.275483	8.122415
H	13.828056	9.275822	9.478161
C	17.210430	9.133879	7.128278
H	18.200922	8.769295	7.406794
C	14.806320	9.234295	7.581767
C	16.101426	8.803481	7.908366
H	16.238098	8.174731	8.791804
C	17.046702	9.912063	5.980893
H	17.903774	10.164452	5.354882
C	13.304049	11.745135	1.956066
H	13.188883	11.202060	1.018273
C	14.652297	10.022412	6.416013
C	10.702369	9.311778	4.976149
C	10.029797	8.120877	4.573413
H	8.969297	8.189299	4.322135
C	12.082823	9.235361	5.306352
C	9.901272	10.575565	5.015216
H	9.328473	10.646858	4.075701
H	10.557092	11.452581	5.060336
C	12.734425	8.010358	5.185224
H	13.800484	7.942238	5.402591
C	8.911583	10.593472	6.199235
H	8.327849	11.522696	6.175226
H	9.453380	10.546744	7.154126
H	8.212464	9.748198	6.158127
C	10.686125	6.903091	4.469765
H	10.149444	6.010254	4.147844
C	12.048128	6.843430	4.771113
H	12.593778	5.902435	4.687322
C	13.476085	7.316742	8.631370
H	13.255585	6.845406	7.663928
H	12.642917	7.096452	9.311575
H	14.374778	6.834298	9.037616
Au	12.079673	11.850705	7.623011
N	10.944553	12.684200	9.139456
C	10.324300	13.239898	9.947278
C	9.549029	13.927892	10.953729
H	9.225005	14.902072	10.561894
H	10.155777	14.08412	11.856807
H	8.662400	13.33342	11.215808

Table S12 Geometry data of **2** for the optimized T_1 state

Au	14.778770	12.994131	7.737425
P	13.904553	14.154919	5.951288
C	13.782053	13.779489	3.215497
H	14.025371	14.840572	3.196344
C	11.160818	14.534136	5.575468
H	11.315260	13.945401	4.671173
C	13.631798	13.129363	4.457778
N	16.096271	12.275207	9.173478
C	13.195998	16.024473	8.499409
H	14.138633	15.543927	8.195726
H	12.970935	15.618416	9.499502

C	9.685436	15.740633	7.048547
H	8.688306	16.102435	7.305746
C	12.075792	15.626228	7.565080
C	10.773748	16.058522	7.860421
H	10.616615	16.673441	8.750015
C	9.878755	14.975019	5.897541
H	9.038554	14.731338	5.245771
C	13.619598	13.115215	2.003687
H	13.743295	13.658945	1.066406
C	12.259165	14.844450	6.398666
C	16.219375	15.538191	4.984819
C	16.900352	16.716733	4.562851
H	17.961772	16.638802	4.318103
C	14.835899	15.626812	5.303504
C	17.010950	14.269037	5.057862
H	17.569362	14.158083	4.112998
H	16.351475	13.397207	5.145221
C	14.189753	16.852077	5.156265
H	13.123168	16.929672	5.368525
C	18.014217	14.281048	6.229493
H	18.596344	13.350590	6.223350
H	17.483503	14.352927	7.188092
H	18.714384	15.123279	6.156115
C	16.250222	17.935425	4.434455
H	16.792687	18.819976	4.099611
C	14.886550	18.007924	4.729497
H	14.349080	18.952603	4.633942
C	16.687881	11.671354	9.974214
C	17.408085	10.914914	10.973848
H	18.030347	10.156362	10.478771
H	16.706490	10.415229	11.657754
H	18.060024	11.581582	11.555858
C	13.411957	17.539803	8.607921
H	13.697980	17.972709	7.639769
H	14.212479	17.761325	9.325876
H	12.504712	18.056636	8.947920
P	13.009647	10.717681	5.951288
C	13.132147	11.093111	3.215497
H	12.888829	10.032028	3.196344
C	15.753382	10.338464	5.575468
H	15.598940	10.927199	4.671173
C	13.282402	11.743237	4.457778
C	13.718202	8.848127	8.499409
H	12.775567	9.328673	8.195726
H	13.943265	9.254184	9.499502
C	17.228764	9.131967	7.048547
H	18.225894	8.770165	7.305746
C	14.838408	9.246372	7.565080
C	16.140452	8.814078	7.860421
H	16.297585	8.199159	8.750015
C	17.035445	9.897581	5.897541
H	17.875646	10.141262	5.245771
C	13.294602	11.757385	2.003687
H	13.170905	11.213655	1.066406
C	14.655035	10.028150	6.398666
C	10.694825	9.334409	4.984819
C	10.013848	8.155867	4.562851
H	8.952428	8.233798	4.318103
C	12.078301	9.245788	5.303504
C	9.903250	10.603563	5.057862
H	9.344838	10.714517	4.112998
H	10.562725	11.475393	5.145221
C	12.724447	8.020523	5.156265
H	13.791032	7.942928	5.368525
C	8.899983	10.591552	6.229493
H	8.317856	11.522010	6.223350
H	9.430697	10.519673	7.188092
H	8.199816	9.749321	6.156115
C	10.663978	6.937175	4.434455
H	10.121513	6.052624	4.099611
C	12.027650	6.864676	4.729497
H	12.565120	5.919997	4.633942
C	13.502243	7.332797	8.607921
H	13.216220	6.899891	7.639769
H	12.701721	7.111275	9.325876
H	14.409488	6.815964	8.947920
Au	12.135430	11.878469	7.737425
N	10.817929	12.597393	9.173478
C	10.226319	13.201246	9.974214
C	9.506115	13.957686	10.973848
H	8.883853	14.716238	10.478771
H	10.207710	14.457371	11.657754
H	8.854176	13.291018	11.555858

Table S13 Geometry data of **2** for the optimized T_2 state

Au	14.81274784	12.99654590	7.61770456
P	13.90135635	14.14190492	5.84836522
C	13.86317566	13.76543267	3.13663119
H	14.17196423	14.80968554	3.11464932
C	11.16479753	14.50662250	5.58313846
H	11.31266522	13.90533346	4.68481356
C	13.67261049	13.13253306	4.39275828
N	15.98448569	12.17910124	9.12965325
C	13.24530697	16.03497990	8.45626339
H	14.16779907	15.49547964	8.19048235
H	12.99172794	15.69849816	9.47592012
C	9.71495026	15.74534384	7.06071445
H	8.72302663	16.11541600	7.32651951
C	12.11497018	15.63418024	7.53681148
C	10.81750607	16.07816521	7.84619714
H	10.67848611	16.71220864	8.72593673
C	9.88694172	14.95239377	5.92290142
H	9.03485077	14.69785285	5.29079537
C	13.66777021	13.11182363	1.93388404
H	13.83165596	13.64212957	0.99583384
C	12.27781615	14.83698693	6.37674501
C	16.24417826	15.57875310	5.07366393

C	16.90093434	16.77516598	4.68037816
H	17.97775222	16.73865156	4.50025278
C	14.85695692	15.63059271	5.31158332
C	17.07442072	14.33050709	5.18826550
H	17.67400271	14.22828183	4.26890662
H	16.43060524	13.44298788	5.23743823
C	14.17067251	16.84126909	5.10601649
H	13.09006563	16.87527052	5.24778595
C	18.01725393	14.37091214	6.40424025
H	18.60401087	13.44377076	6.45374176
H	17.44710065	14.46844652	7.33913806
H	18.71841628	15.21371445	6.34449042
C	16.21475317	17.97778691	4.49110117
H	16.75547540	18.87227475	4.17971002
C	14.84172681	18.01266151	4.69789966
H	14.27644864	18.93451910	4.55490433
C	16.63603134	11.66151697	9.93850171
C	17.44901459	11.0178959	10.94500502
H	17.75226695	10.02292713	10.58995702
H	16.87911142	10.91083849	11.87890768
H	18.34867762	11.61859669	11.14058921
C	13.52445107	17.54303216	8.48516958
H	13.87637385	17.89744226	7.50624336
H	14.29760950	17.77635303	9.22892581
H	12.62460271	18.11851783	8.74206531
P	13.01284365	10.73069508	5.84836522
C	13.05102434	11.10716733	3.13663119
H	12.74223577	10.0629144	3.11464932
C	15.74940247	10.36597750	5.58313846
H	15.60153478	10.96726654	4.68481356
C	13.24158951	11.74006694	4.39275828
C	13.66889303	8.83762010	8.45626339
H	12.74640093	9.37712036	8.19048235
H	13.92247206	9.17410184	9.47592012
C	17.19924974	9.12725616	7.06071445
H	18.19117337	8.75718400	7.32651951
C	14.79922982	9.23841976	7.53681148
C	16.09669393	8.79443479	7.84619714
H	16.23571389	8.16039136	8.72593673
C	17.02725828	9.92020623	5.92290142
H	17.87934923	10.17474715	5.29079537
C	13.24642979	11.76077637	1.93388404
H	13.08254404	11.23047043	0.99583384
C	14.63638385	10.03561307	6.37674501
C	10.67002174	9.29384690	5.07366393
C	10.01326566	8.09743402	4.68037816
H	8.93644778	8.13394844	4.50025278
C	12.05724308	9.24200729	5.31158332
C	9.83977928	10.54209291	5.18826550
H	9.24019729	10.64431817	4.26890662
H	10.48359476	11.42961212	5.23743823
C	12.74352749	8.03133091	5.10601649
H	13.82413437	7.99732948	5.24778595
C	8.89694607	10.50168786	6.40424025
H	8.31018913	11.42882924	6.45374176
H	9.46709935	10.40415348	7.33913806
H	8.19578372	9.65888555	6.34449042
C	10.69944683	6.89481309	4.49110117
H	10.15872460	6.00032525	4.17971002
C	12.07247319	6.85993849	4.69789966
H	12.63775136	5.93808090	4.55490433
C	13.38974893	7.32956784	8.48516958
H	13.03782615	6.97515774	7.50624336
H	12.61659050	7.09624697	9.22892581
H	14.28959729	6.75408217	8.74206531
Au	12.10145216	11.87605410	7.61770456
N	10.92971431	12.69349876	9.12965325
C	10.27816866	13.21108303	9.93850171
C	9.46518541	13.85470402	10.94500502
H	9.16193305	14.84967287	10.58995702
H	10.03508858	13.96176151	11.87890768
H	8.56552238	13.25400331	11.14058921

Table S14 Geometry data of **3** for the optimized S_1 state

Au	19.672359	6.575192	6.277153
P	20.719676	7.628045	4.542535
N	18.529591	5.758472	7.784393
C	21.377624	8.925803	8.513959
C	23.444960	7.981090	4.336770
C	21.310740	9.595586	7.131671
C	18.371392	9.043126	3.582622
C	20.917715	7.266509	1.836972
C	23.774463	9.565490	6.593891
C	24.886653	9.192027	5.837759
C	20.366958	10.357462	3.877981
C	19.755521	9.124446	3.955568
C	21.041478	6.579232	0.648057
C	22.475037	9.159674	6.254472
C	24.724047	8.394603	4.703549
C	20.923817	6.618959	3.107310
C	22.322472	8.353137	5.100522
C	17.105842	7.469804	2.113338
C	17.670780	10.249968	3.199629
C	19.656766	11.538230	3.481051
C	18.297421	11.476822	3.150738
C	17.606624	7.765182	3.547283
C	17.135681	4.421399	9.529154
C	16.431119	7.814874	4.553956
C	21.224399	11.122837	7.272330
C	17.906912	5.157057	8.555538
P	21.423187	4.163600	4.580796
C	20.836266	2.901734	8.570221
C	18.665885	3.878666	4.450934
C	20.865595	2.246673	7.179604
C	23.751220	2.804216	3.715642
C	21.271325	4.507834	1.883331
C	18.388538	2.286686	6.705345

C	17.257310	2.661713	5.978351
C	21.700898	1.475266	3.882705
C	22.376545	2.698526	4.035087
C	21.199613	5.166025	0.670276
C	19.680052	2.695273	6.338514
C	17.393948	3.463632	4.844096
C	21.172473	5.174083	3.132669
C	19.806375	3.507975	5.186265
C	25.041190	4.540039	2.409910
C	24.406433	1.642429	3.281715
C	22.375591	0.342218	3.434307
C	23.738288	0.426826	3.142962
C	24.531370	4.105892	3.791749
C	25.666662	4.025029	4.822172
C	20.951627	0.717774	7.297285
Au	22.433710	5.287733	6.308588
N	23.631671	6.091406	7.803748
C	25.298548	7.136936	9.508587
C	24.373788	6.558701	8.561467
H	21.390178	7.830935	8.424364
H	20.509505	9.214383	9.122448
H	22.282612	9.238473	9.055184
H	23.302282	7.358556	3.452108
H	20.376925	9.251109	6.657504
H	20.814082	8.350246	1.791492
H	23.918922	10.204550	7.467747
H	25.880813	9.537859	6.126979
H	21.427675	10.448109	4.114142
H	21.024263	7.120569	-0.297530
H	25.585288	8.102905	4.100986
H	16.400088	8.228117	1.748231
H	16.578139	6.507175	2.131008
H	17.945176	7.393182	1.412364
H	16.616598	10.167594	2.936002
H	20.192875	12.487472	3.435577
H	17.755119	12.374680	2.855014
H	18.271547	6.948182	3.845633
H	16.133014	4.215018	9.129839
H	17.043499	5.008447	10.453613
H	17.638047	3.469811	9.751931
H	16.791820	7.996646	5.574693
H	15.928369	6.839269	4.530700
H	15.688462	8.582083	4.298204
H	20.326618	11.403191	7.840004
H	21.183297	11.626467	6.296613
H	22.093128	11.527338	7.809766
H	20.810400	3.998628	8.496624
H	21.728143	2.616177	9.144820
H	19.957051	2.568288	9.142134
H	18.796989	4.474808	3.545847
H	21.786416	2.583831	6.678122
H	21.431218	3.429361	1.882211
H	18.268498	1.629839	7.569893
H	16.271874	2.302929	6.281818
H	20.635149	1.414092	4.103330
H	21.287887	4.602781	-0.258200
H	16.519200	3.738391	4.252457
H	25.754641	3.812330	1.998312
H	25.560866	5.506582	2.483125
H	24.212695	4.645756	1.697107
H	25.468333	1.694426	3.034367
H	21.838727	-0.599168	3.309924
H	24.281010	-0.454181	2.796849
H	23.838889	4.893314	4.133731
H	25.282308	3.750222	5.815293
H	26.176251	4.996091	4.904186
H	26.418553	3.276908	4.534987
H	21.852792	0.434890	7.858269
H	21.003591	0.241141	6.310734
H	20.085106	0.303548	7.831983
H	26.282589	7.262394	9.035593
H	25.401469	6.475474	10.380181
H	24.928864	8.116871	9.841158

Table S15 Geometry data of **3** for the optimized T_1 state

Au	19.835980	6.527227	6.210141
P	20.778902	7.658883	4.427638
N	18.597202	5.770669	7.744410
C	21.497765	8.963554	8.423432
C	23.511191	7.905671	4.214852
C	21.421616	9.580113	7.017078
C	18.330406	8.964467	3.843971
C	20.673901	7.250093	1.746532
C	23.881032	9.496753	6.464907
C	24.981243	9.097531	5.704922
C	20.383895	10.310833	3.762409
C	19.733077	9.085775	4.011356
C	20.867648	6.592546	0.550189
C	22.571999	9.111493	6.138149
C	24.798885	8.297953	4.573746
C	20.877367	6.618025	3.007129
C	22.402430	8.303251	4.986414
C	16.996028	7.118215	2.761738
C	17.630965	10.102076	3.417158
C	19.661287	11.418340	3.333230
C	18.276572	11.312691	3.168783
C	17.559768	7.676889	4.073760
C	16.896841	4.690494	9.391340
C	16.473418	7.834385	5.146852
C	21.348250	11.112333	7.098109
C	17.836609	5.289579	8.474469
P	21.390127	4.169024	4.428457
C	20.670690	2.861804	8.423409
C	18.657389	3.927105	4.216166
C	20.744910	2.246727	7.016308
C	23.836672	2.859032	3.845079
C	21.496642	4.576700	1.747181
C	18.285347	2.335436	6.465442

C	17.185610	2.737255	5.706125
C	21.780960	1.515949	3.766044
C	22.433870	2.740249	4.013268
C	21.303332	5.233796	0.550518
C	19.594976	2.718533	6.138517
C	17.369071	3.537136	4.575331
C	21.292907	5.209309	3.007449
C	19.765628	3.527176	4.987251
C	25.173346	4.701219	2.758919
C	24.534030	1.719738	3.419340
C	22.501549	0.406698	3.337973
C	23.886346	0.509867	3.172775
C	24.609675	4.145636	4.072274
C	25.696536	3.988033	5.144821
C	20.815440	0.714276	7.095424
Au	22.333710	5.301184	6.210281
N	23.571505	6.057216	7.745468
C	25.268947	7.134860	9.397044
C	24.330802	6.536998	8.477716
H	21.491738	7.865000	8.384808
H	20.641025	9.291658	9.027814
H	22.411012	9.285553	8.945494
H	23.348480	7.300579	3.321470
H	20.479583	9.235550	6.560245
H	20.369138	8.296487	1.728255
H	24.040837	10.146237	7.328269
H	25.982570	9.432831	5.981818
H	21.465596	10.381433	3.876683
H	20.697729	7.118161	-0.388979
H	25.651298	8.005235	3.959244
H	16.272386	7.816099	2.316479
H	16.469474	6.171173	2.945020
H	17.793027	6.941313	2.028044
H	16.550594	10.039432	3.277024
H	20.175270	12.356311	3.119652
H	17.696611	12.178339	2.844859
H	18.279527	6.919560	4.456381
H	15.928593	4.552213	8.890031
H	16.761419	5.342072	10.266061
H	17.276629	3.713623	9.722288
H	16.890288	8.224265	6.086590
H	16.001554	6.862457	5.349550
H	15.683386	8.523731	4.819021
H	20.472252	11.416523	7.687001
H	21.263619	11.565927	6.102999
H	22.238483	11.531546	7.587784
H	20.678715	3.960387	8.386051
H	21.527164	2.531416	9.026925
H	19.757160	2.540896	8.945643
H	18.820929	4.532543	3.323166
H	21.687350	2.590033	6.559354
H	21.801298	3.530267	1.729404
H	18.124654	1.685580	7.328362
H	16.183752	2.403659	5.983164
H	20.699227	1.447167	3.881156
H	21.473507	4.707804	-0.388392
H	16.516986	3.831912	3.961353
H	25.895477	4.001374	2.314285
H	25.701640	5.647668	2.940225
H	24.376089	4.878216	2.025525
H	25.614424	1.780459	3.278535
H	21.985931	-0.530714	3.125894
H	24.464754	-0.357133	2.849692
H	23.891477	4.904843	4.454208
H	25.279698	3.600373	6.085488
H	26.170217	4.959473	5.345611
H	26.485142	3.296809	4.817509
H	21.691212	0.407711	7.683419
H	20.898625	0.261765	6.099693
H	19.924711	0.296137	7.585116
H	26.236959	7.277362	8.896462
H	25.405773	6.480333	10.269341
H	24.886721	8.109552	9.731616

Table S16 Geometry data of **3** for the optimized T_2 state

Au	19.93615018	5.87846956	6.80698795
P	21.34709280	7.69207304	6.62687596
N	18.28865294	4.70512805	7.27483171
C	22.03328171	4.87009019	9.64630422
H	21.76081231	4.36862720	8.70704984
H	21.21981791	4.71935642	10.36923760
H	22.93398150	4.38938034	10.05670435
C	24.08759979	7.40914815	6.16618537
H	23.86769437	7.89536144	5.21536760
C	22.27398324	6.37205667	9.42148334
H	21.32258805	6.79918991	9.06197887
C	19.67323937	9.76294103	7.67722091
C	21.70403092	9.76213611	4.83289053
H	21.86752700	10.33683944	5.74329653
C	24.65115395	6.20190458	8.60040487
H	24.89094118	5.74570696	9.56328736
C	25.66956383	6.38300491	7.66460458
H	26.68714209	6.06536131	7.89917654
C	21.97391130	9.75320265	8.45389500
H	22.98450557	9.34434218	8.42421154
C	20.97894323	9.19415559	7.65565287
C	21.75081605	10.42797449	3.61129667
H	21.94814811	11.50048120	3.58506814
C	23.33040239	6.60523183	8.35231151
C	25.38856937	6.99177211	6.44055362
H	26.18062927	7.15465516	5.70807505
C	21.45730763	8.37657299	4.92841265
C	23.05648287	7.21671154	7.10416849
C	18.07932572	10.38396772	5.83163503
H	17.65444549	11.24336029	6.36825561
H	17.29372186	9.98005844	5.17799788
H	18.90434938	10.74342854	5.20262041
C	19.42341733	10.85560741	8.55632257

H	18.42082940	11.28513769	8.58191012
C	21.70279918	10.84742767	9.30860126
H	22.50291733	11.25539047	9.92833548
C	20.41717042	11.39354487	9.36084664
H	20.20011156	12.23498332	10.01962285
C	18.55274887	9.27850477	6.79610390
H	18.93024689	8.44725252	6.18364780
C	16.45213026	2.85136302	7.35414498
H	15.46041795	3.28129754	7.15511588
H	16.44220183	2.38857195	8.35111036
H	16.66800019	2.07639891	6.60382556
C	17.38769151	8.72852320	7.64199067
H	17.72397899	7.90971533	8.29193814
H	16.60892616	8.33929959	6.97173202
H	16.93319872	9.50752474	8.26919355
C	22.62164908	7.07415847	10.74275613
H	21.80957115	6.93492909	11.46949356
H	22.77404483	8.15291049	10.60548917
H	23.53850600	6.66184755	11.18716813
C	17.46132398	3.88525539	7.30895407
P	21.05467800	5.82051843	3.59853885
C	19.46516710	2.10714292	4.69050356
H	19.74255061	2.68695198	5.58209727
H	20.14169319	1.24498083	4.61259382
H	18.44533023	1.71636815	4.82476246
C	18.38764833	6.64615690	3.70892031
H	18.81253249	7.65008367	3.72717998
C	19.55331486	2.96957153	3.42043935
H	20.60649510	3.28069697	3.31674839
C	22.96956715	5.41506841	1.51110905
C	21.31671973	8.33931773	2.49715399
H	21.15770685	7.79502022	1.56741871
C	17.30623899	4.09204564	3.62933138
H	16.86642175	3.09376760	3.57692459
C	16.46441192	5.19709355	3.75506175
H	15.38329349	5.05505334	3.80421401
C	20.63791269	5.15549758	0.88460071
H	19.57692600	5.20833185	1.13110196
C	21.58858078	5.45090268	1.85856459
C	21.53899045	9.71199947	2.43212169
H	21.55011748	10.21482224	1.46420552
C	18.70086108	4.22258675	3.54830311
C	17.00641187	6.48264822	3.79520754
H	16.35698961	7.35554840	3.87706611
C	21.28520233	7.63679546	3.71993825
C	19.23942047	5.53205949	3.59329131
C	24.84526720	7.02729020	1.96656838
H	25.36269401	6.82652076	1.01846335
H	25.60778781	7.30045308	2.70920264
H	24.17826907	7.88707749	1.82044930
C	23.32681592	5.02659237	0.18814092
H	24.38455834	4.9883853	-0.07632391
C	21.01897505	4.78496710	-0.42621852
H	20.24888146	4.55019728	-1.16281165
C	22.37248142	4.71462362	-0.76889499
H	22.67361834	4.42646766	-1.77655020
C	24.06661418	5.79528053	2.46980997
H	23.60610472	6.06686272	3.43041440
C	25.00546783	4.60267650	2.73574338
H	24.44984851	3.74514826	3.13812366
H	25.76361891	4.89943264	3.47356734
H	25.52981725	4.28245859	1.82511776
C	19.19370152	2.14638802	2.17436060
H	19.86956903	1.28511650	2.08281495
H	19.27297603	2.74021007	1.25414016
H	18.16734204	1.75741993	2.23265603
Au	22.04102173	4.63304896	5.31060684
N	23.34334556	3.39512408	6.34944778
C	24.74589518	2.17191165	8.18036346
H	25.82081556	2.32337511	8.00854086
H	24.53208964	1.09420204	8.14671030
H	24.48058270	2.55667442	9.17623371
C	23.97789596	2.85106295	7.16140134

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