Electronic Supplementary Information for:

Electron-density distribution tuning for enhanced thermal stability of luminescent gold complexes

Shigeyuki Yamada,[a,b] Shun Yamaguchi[a] and Osamu Tsutsumi[a*]

[a] *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University. 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan.*

[b] *Present address: Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.*

* Correspondence should be addressed to O. Tsutsumi.
Phone: +81-77-561-5966, Fax: +81-77-561-2659, E-mail: tsutsumi@sk.ritsumei.ac.jp

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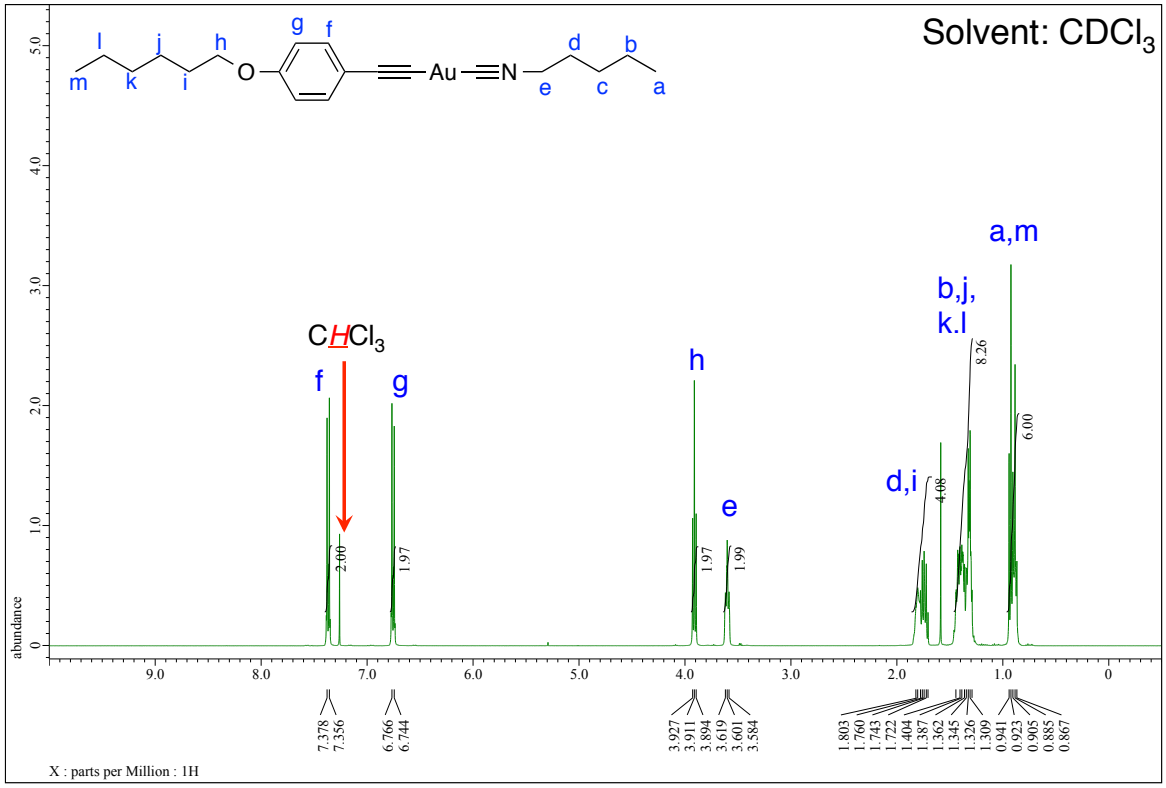
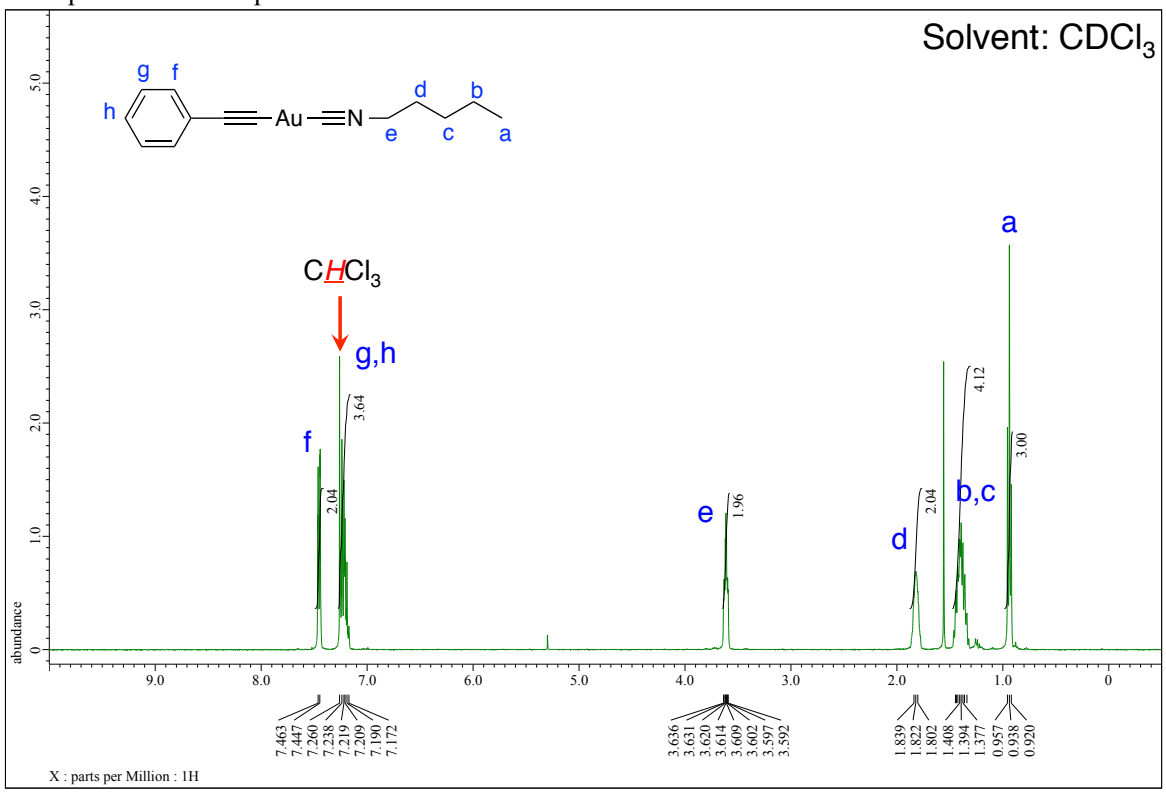
1. NMR spectra of gold complexes

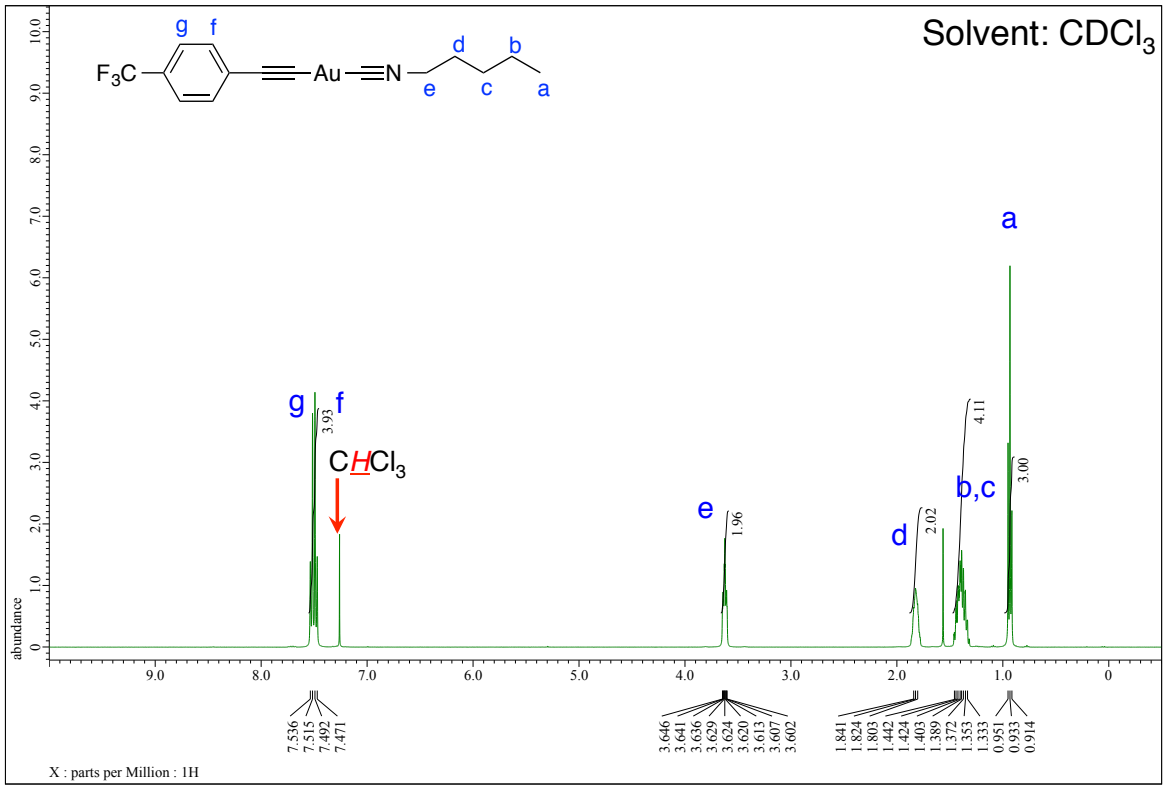
^{1}H NMR spectrum of complex **1**



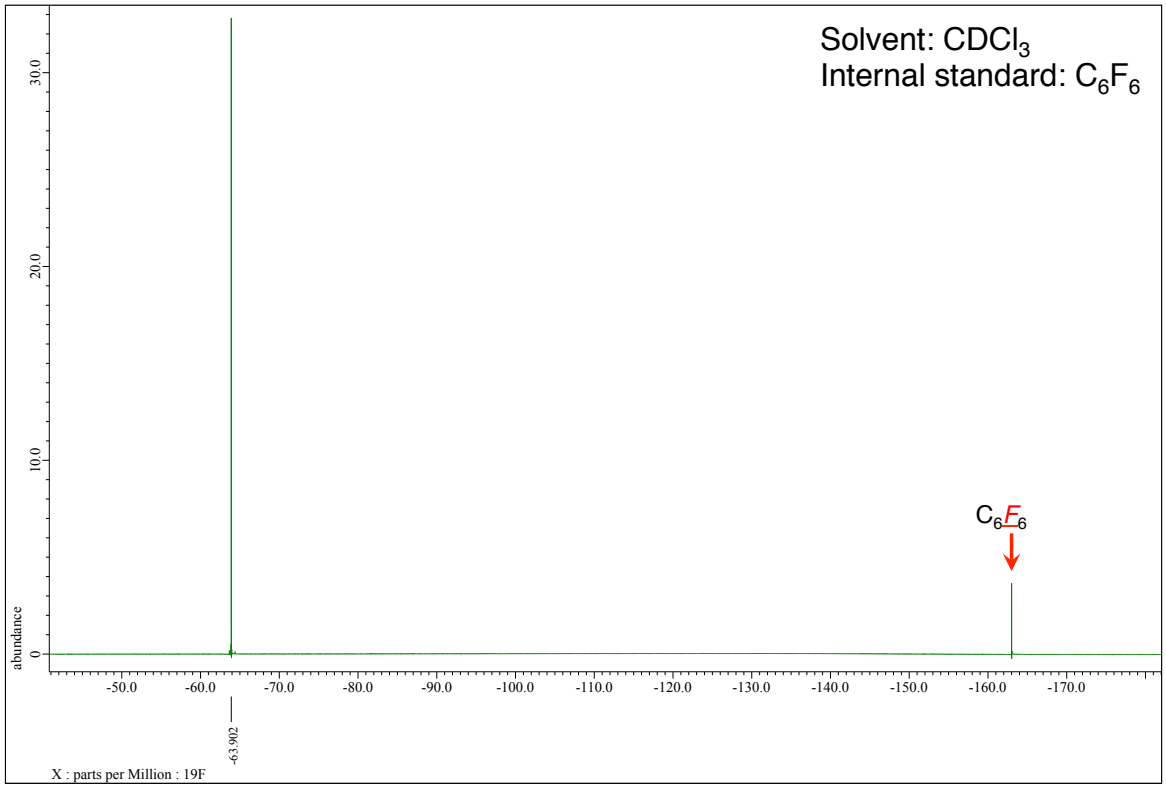
^{1}H NMR spectrum of complex **2**



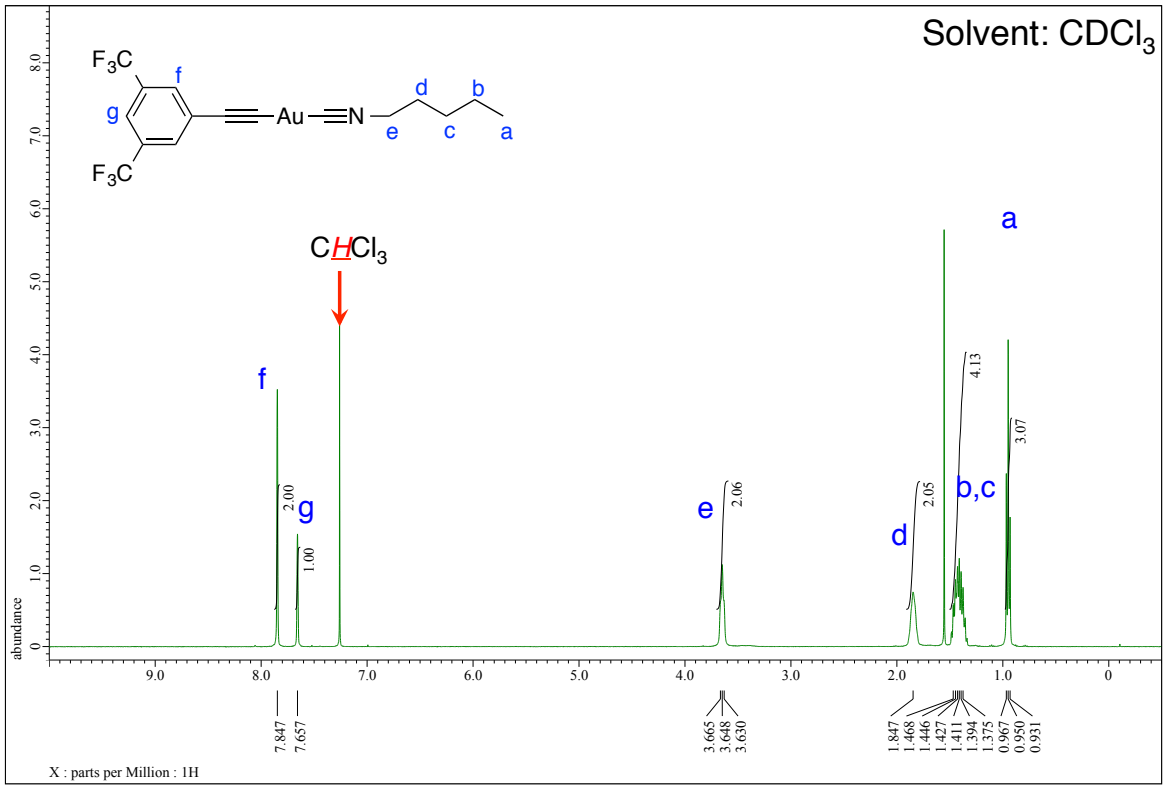
^{1}H NMR spectrum of complex **3**



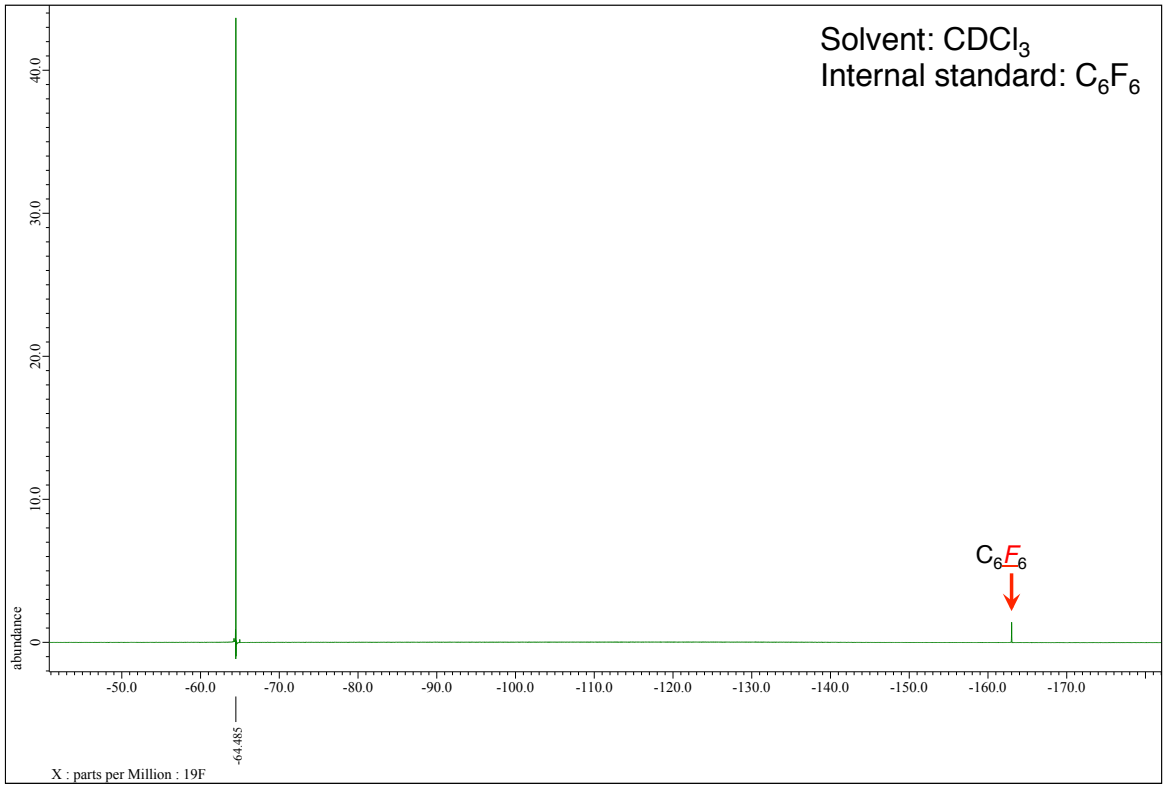
^{19}F NMR spectrum of complex **3**



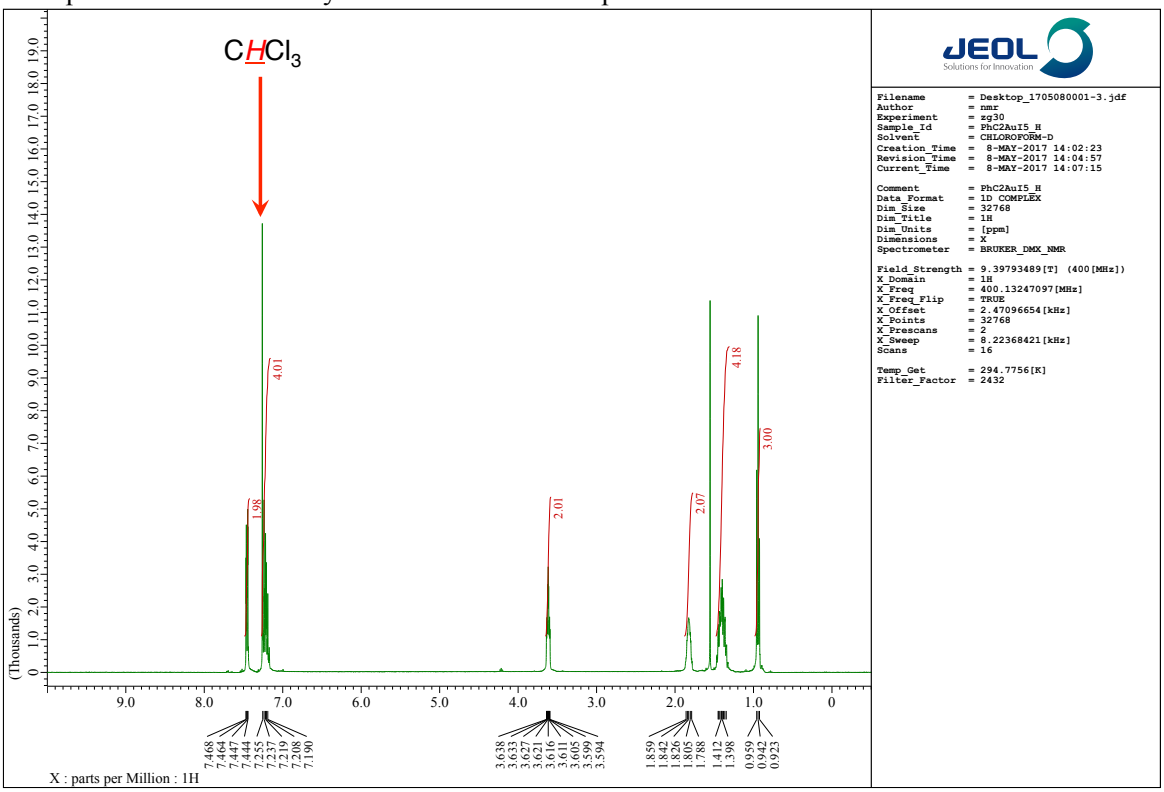
^{1}H NMR spectrum of complex **4**



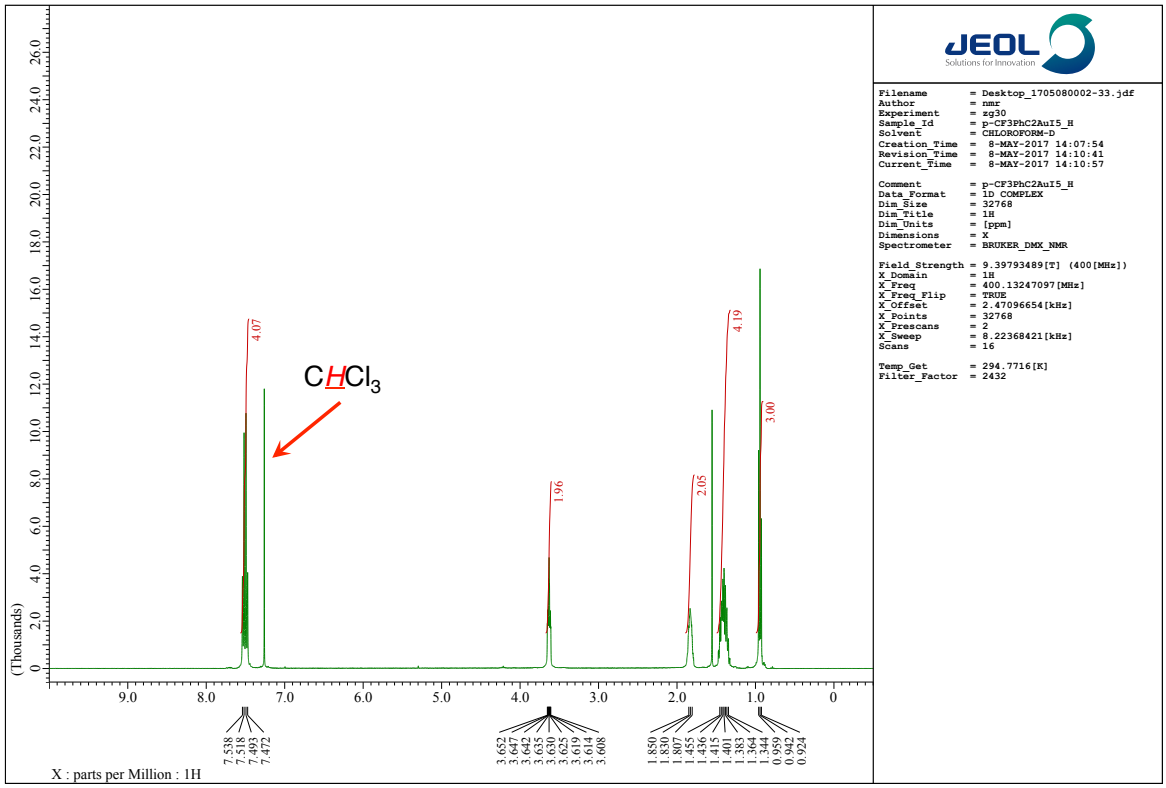
^{19}F NMR spectrum of complex **4**



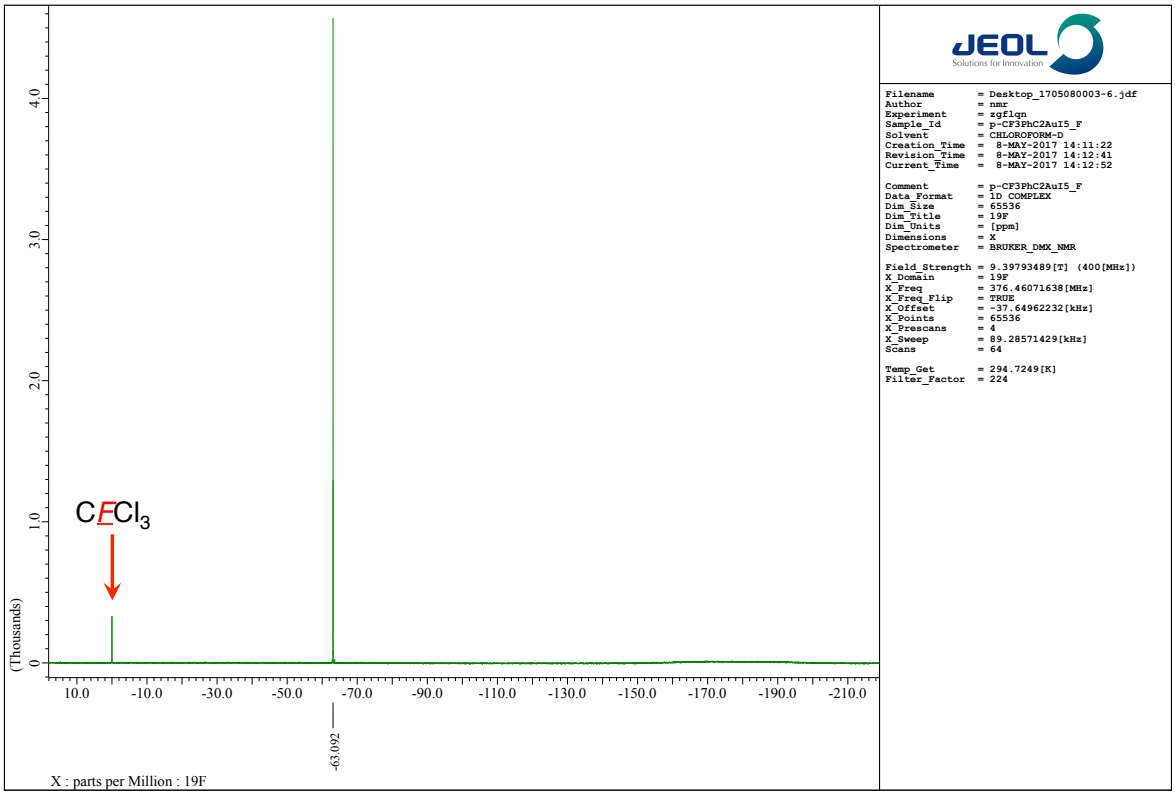
^{1}H NMR spectrum of **2** after >1 year stored at room temperature in air



^{1}H NMR spectrum of **3** after >1 year stored at room temperature in air



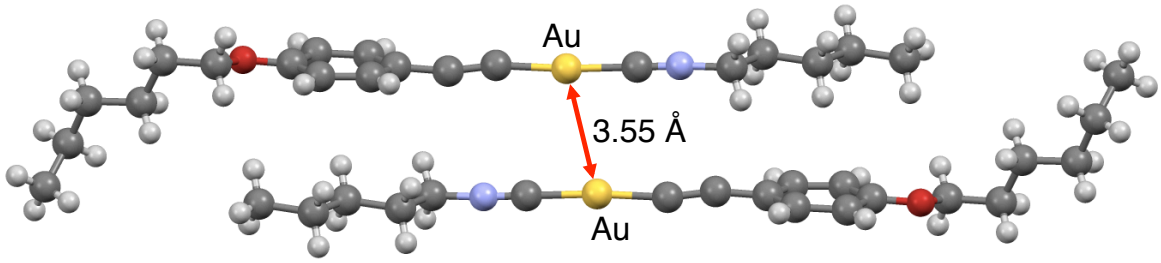
^{19}F NMR spectrum of **3** after >1 year stored at room temperature in air



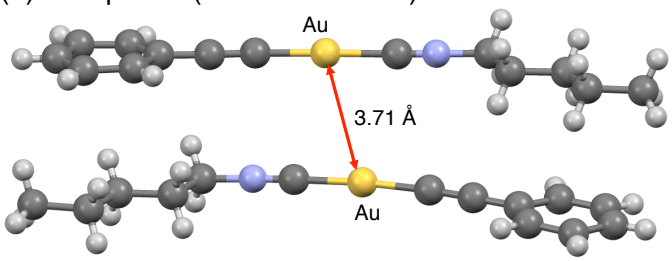
2. X-Ray Crystallography

Single crystals were obtained by slow evaporation from a mixed solvent system of hexane and dichloromethane. The X-ray diffraction measurement was carried out at room temperature (296 K). The crystal packing of new gold complexes **2** and **3**, together with reported **1**, are shown in Fig. S1. The crystal data of the novel complexes **2** and **3** disclosed in Table 1 have been indexed, and are included in the Cambridge Crystallographic Center (CCDC) database with the following reference numbers: CCDC 1435643 for **2** and 1429452 for **3**. The indexed database contains additional supplementary crystallographic data for this paper and may be accessed without charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html. The CCDC may be contacted by mail at 12 Union Road, Cambridge CB2 1EZ, U.K., by fax at (44) 1223-336-033, or by e-mail at deposit@ccdc.cam.ac.uk.

(a) Complex **1** (CCDC 927045, reported in *J. Mater. Chem. C*, **2013**, *1*, 5359.)



(b) Complex **2** (CCDC 1435643)



(c) Complex **3** (CCDC 1429452)

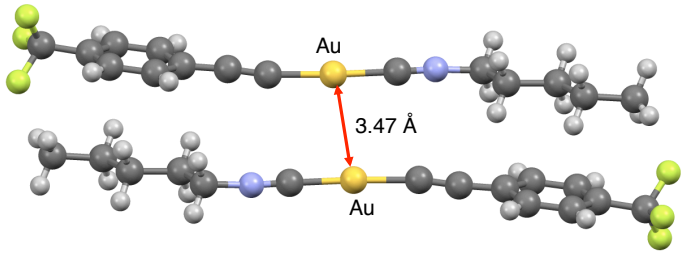


Fig. S1. Crystal packing structures of complexes **1**–**3** and the nearest Au–Au distance. Color legend: grey, carbon; red, oxygen; blue, nitrogen; light green, fluorine; yellow, gold.

Table S1. Crystallographic data for gold complexes **1**–**3**.

Complex	**1**	**2**	**3**
Empirical Formula	$C_{20}H_{28}AuNO$	$C_{14}H_{16}AuN$	$C_{15}H_{15}AuF_3N$
Formula Weight	495.40	395.24	463.25
Temperature [K]	296	298	296
Crystal Color / Habit	Colorless / plate	Colorless / needle	Colorless / plate
Crystal Size [mm]	0.44 × 0.18 × 0.04	0.15 × 0.10 × 0.10	0.10 × 0.05 × 0.05
Crystal System	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a [Å]	7.3596(8)	7.8590(9)	7.7708(15)
b [Å]	9.8116(2)	10.4832(12)	8.3156(17)
c [Å]	13.9641(2)	17.157(2)	12.492(3)
α [°]	89.373(7)	80.866(3)	98.152(4)
β [°]	88.527(9)	80.625(3)	104.868(4)
γ [°]	83.285(6)	85.192(4)	92.540(4)
V [Å^3]	1001.06(16)	1374.5(3)	769.6(3)
Z	2	4	2
R [$F^2 > 2\sigma(F^2)$]	0.045	0.094	0.083
wR(F^2)	0.125	0.286	0.279

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)]/\Sigma w|F_o|\}^{1/2}$.

3. Thermal properties

Thermal stabilities of the new complexes **2**–**4** were evaluated by thermogravimetric analysis (TGA; Shimadzu, DTG-60AH) at a heating rate of 5.0 °C min^{-1} (Fig. S2). Thermal decomposition temperature is defined as the temperature at which 5% weight loss occurred, and this data is summarized in the main text.

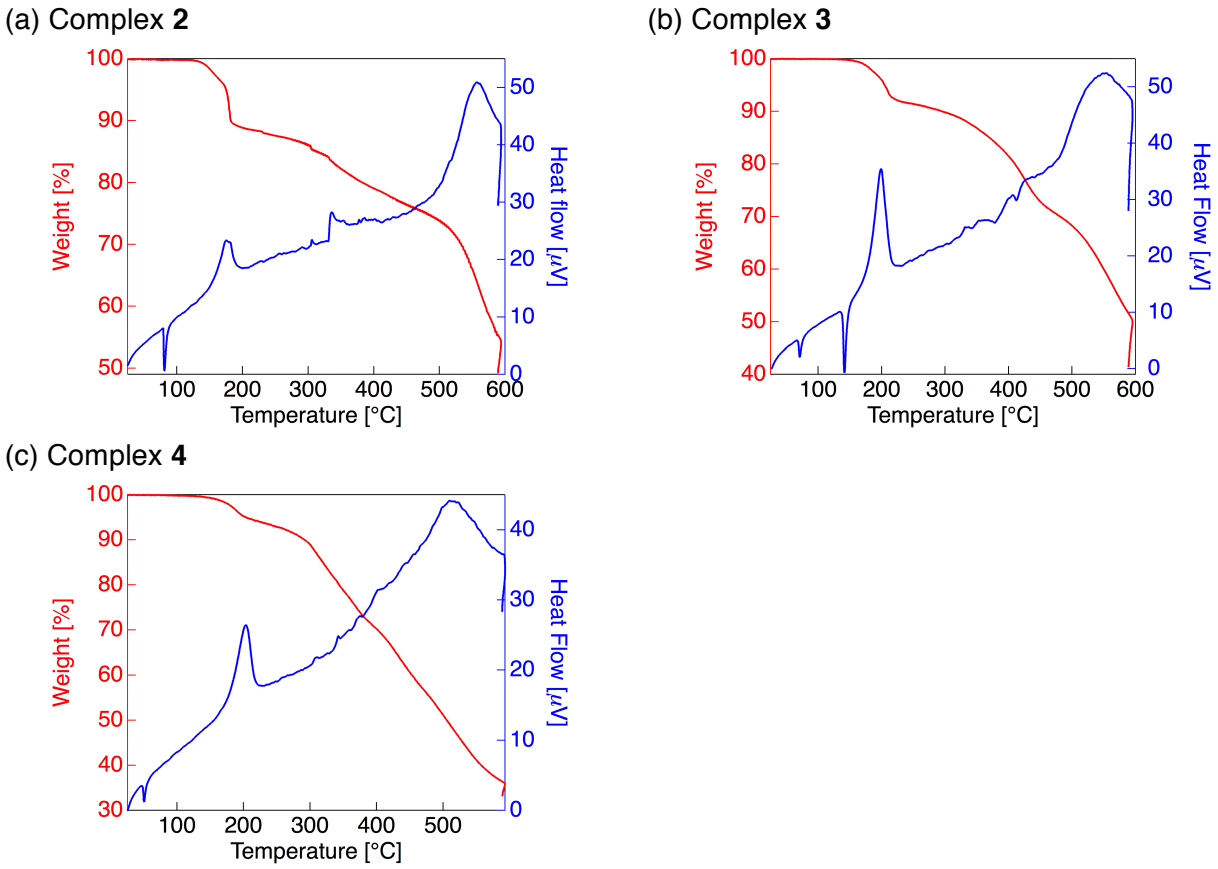
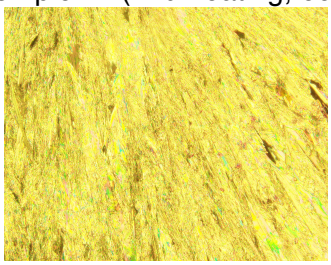


Fig. S2 TG-DTA thermograms of gold complexes **2**–**4** in air. Heating rate was 5.0 °C min^{-1}.

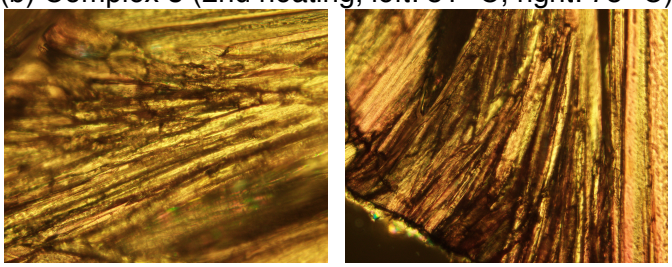
4. Polarized optical microscopy (POM)

Polarized optical microscopy was carried out using an Olympus BX51 microscope equipped with a temperature-controlled stage (Instec HCS302 microscope hot and cold stage and mK1000 temperature controller). The observed optical textures for new gold complexes **2–4** were shown in Fig. S3. The texture for known complex **1** was reported in *J. Mater. Chem. C*, **2013**, *1*, 5359.

(a) Complex **2** (2nd heating, 60 °C)



(b) Complex **3** (2nd heating, left: 51 °C, right: 75 °C)



(c) Complex **4** (2nd heating, left: 33 °C, right: 35 °C)

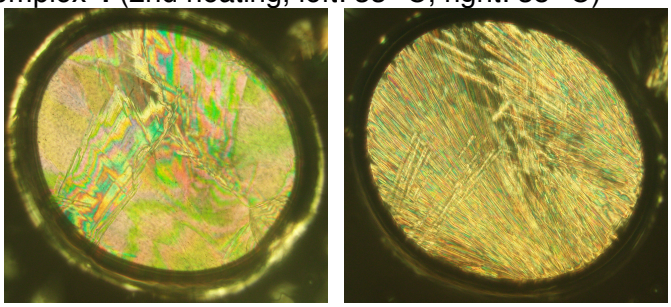


Fig. S3 POM textures of new gold complexes **2–4** in their crystalline (Cry) phase. The optical textures of Cry^1 and Cry^2 of **3** and **4** were taken at the same spots.

5. Phase transition behaviour and the POM texture

Phase transition behaviour of the complexes **2**–**4** were assessed using DSC (SII X-DSC7000) at heating and cooling rates of 2.0 °C min^{-1} (Fig. S4). At least three scans were conducted to check reproducibility. The data is also summarized in the main text. The thermogram for known complex **1** was reported in *J. Mater. Chem. C*, **2013**, *1*, 5359.

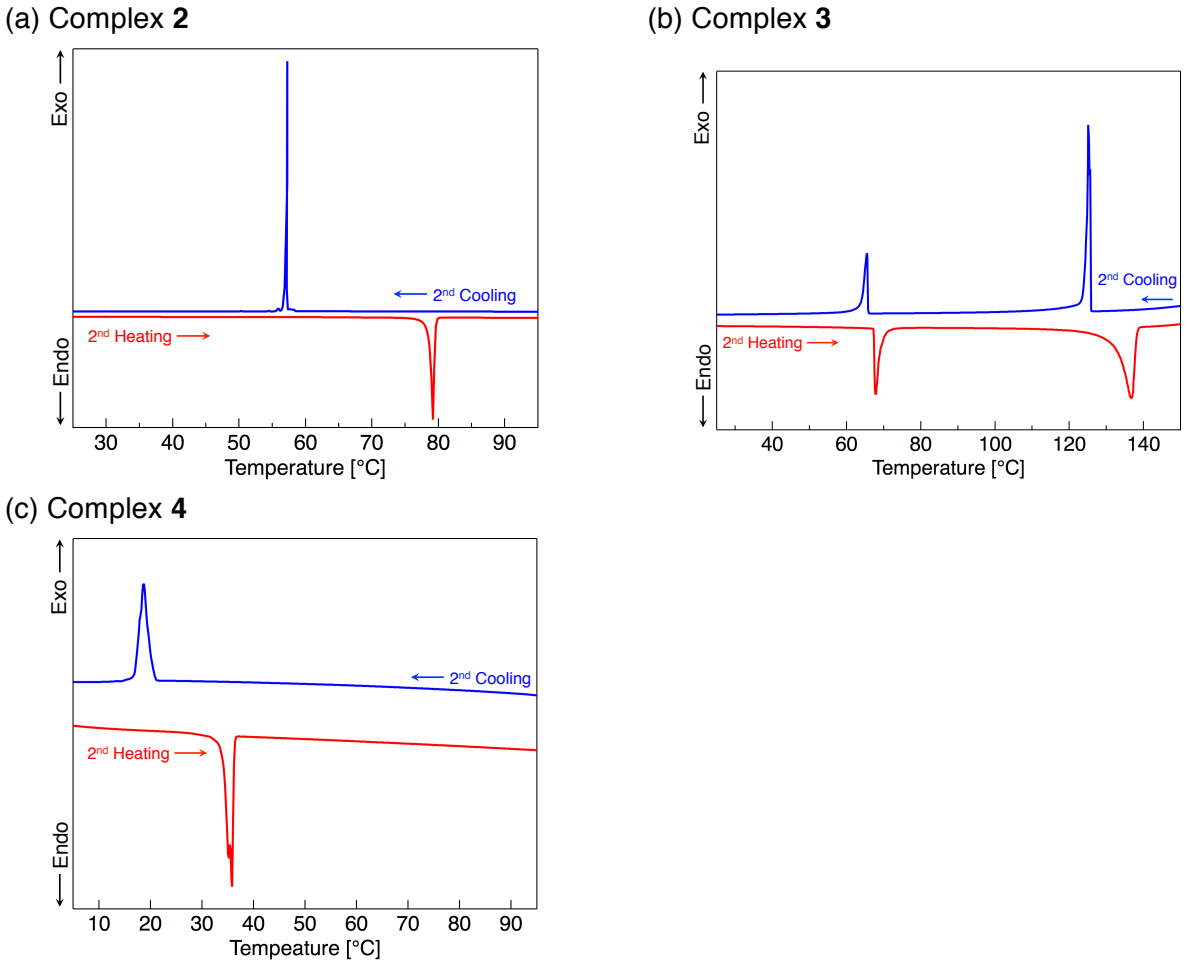
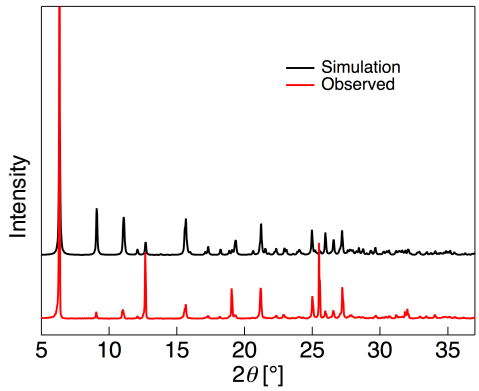


Fig. S4 DSC curves of gold complexes **2**–**4** in nitrogen atmosphere (2nd cycles). Scan rate was 2.0 °C min^{-1}.

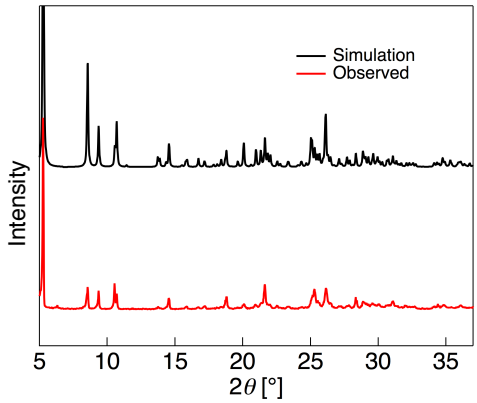
6. Powder X-ray diffraction measurement

Powder XRD measurements for 1–3 at room temperature were carried out using Rigaku Ultima IV with D/tex-Ultra detector and a scintillation counter. For the samples showing a Cry-to-Cry phase transition, namely complexes 3 and 4, the crystal structures were further confirmed by XRD at various temperatures with the same XRD instrument coupled to a DSC setup (Rigaku, Thermo Plus2, DSC8230).

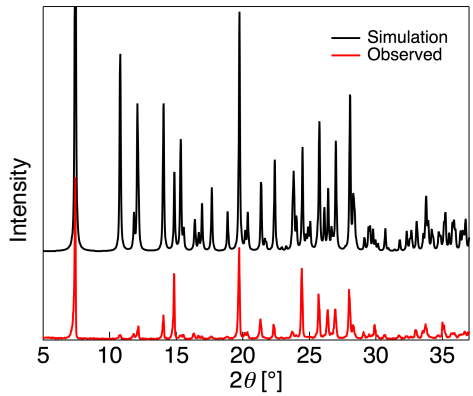
(a) Complex **1** (at 25 °C)



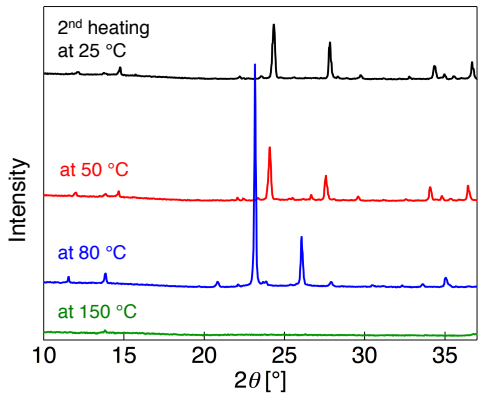
(b) Complex **2** (at 25 °C)



(c) Complex **3** (at 25 °C)



(d) Complex **3** (XRD in 2nd heating)



(e) Complex **4** (XRD in 2nd heating)

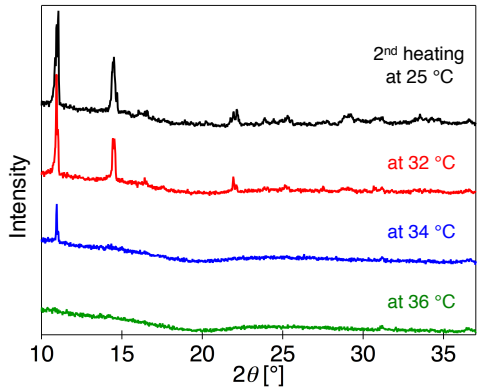
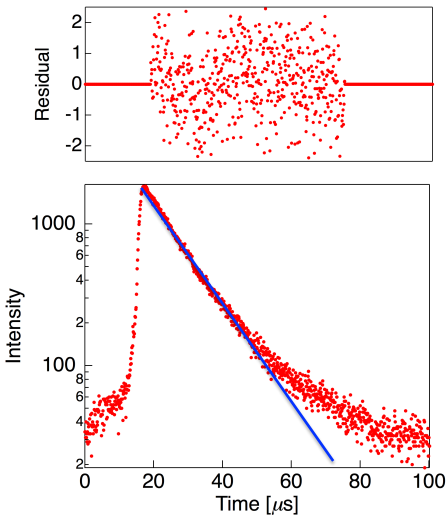


Fig. S5 (a)–(c) XRD pattern of complexes **1**–**3** at 25 °C: black, simulated pattern obtained from the single crystal; red, observed powder XRD pattern. The measurement was performed in a shallow glass dish. While preparing the sample, the crystals were aligned to one direction; thus, the intensity of some particular diffractions were enhanced.
(d), (e) XRD pattern measured at various temperatures for complex **3** (d) and **4** (e). The measurement was performed with an aluminum pan. The undulation of the baseline in the range of $2\theta < \sim 25°$ is due to the pan.

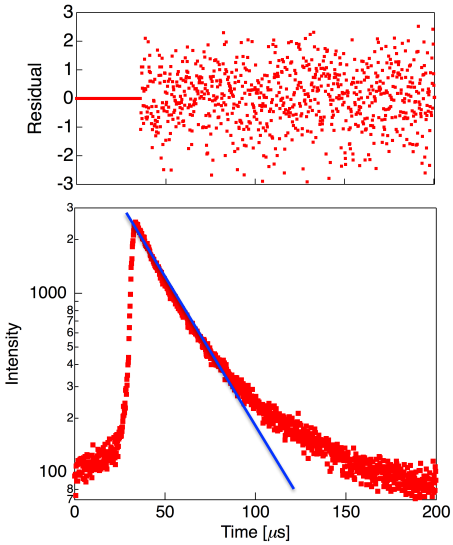
7. Photoluminescence Lifetime

Photoluminescence decay profiles were obtained using a Nd:YAG laser (Continuum, Minilite II, λ = 337 nm; pulse width = 4 ns, FWHM; repetition rate = 10 Hz). The decay profiles were recorded using a streak camera (Hamamatsu, C7700).

(a) Complex 2



(b) Complex 3



(c) Complex 4

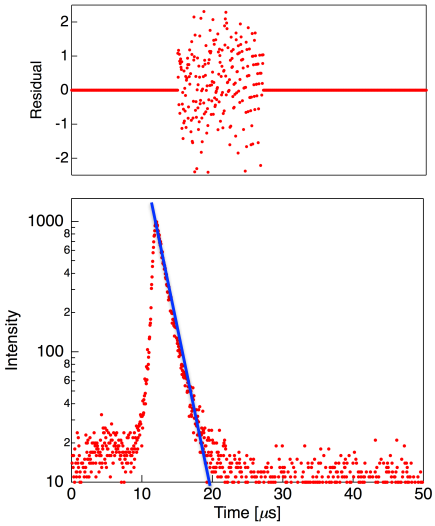


Fig. S6. Photoluminescence decay profiles of gold complexes **2**–**4** observed in a wavelength range of 450–600 nm at room temperature in air. The measurement was carried out using a laser pulse at 355 nm (4 ns, FWHM; 10 Hz).

7. Cartesian coordinates

Computation was carried out by using Gaussian 09W (rev. D.01) using the B3LYP/6-311+G(d,p) levels of theory. The calculations for complexes **1**–**3** were performed with the initial conformation obtained from their crystal structures, whose Cartesian coordinates are listed in Tables S2–S4. The optimized geometry for **4** was calculated using the same basis set, and its Cartesian coordinates are tabulated in Table S5.

Table S2. Cartesian coordinates for complex **1**.

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	Au	0	2.586394	-0.496892	0.178717
2	C	0	11.514662	1.985502	-0.468366
3	H	0	11.815843	2.005774	0.573782
4	H	0	11.938801	2.857742	-0.951871
5	H	0	11.956965	1.106303	-0.925058
6	C	0	9.989975	1.969409	-0.602265
7	H	0	9.718267	1.982594	-1.654249
8	H	0	9.578179	2.875564	-0.166400
9	C	0	9.350215	0.748771	0.070105
10	H	0	9.763718	-0.157172	-0.367415
11	H	0	9.623085	0.737520	1.122987
12	C	0	7.823773	0.734798	-0.065561
13	H	0	7.543726	0.735008	-1.113366
14	H	0	7.402986	1.630710	0.377838
15	C	0	7.214493	-0.493439	0.614684
16	H	0	7.588282	-1.407008	0.173473
17	H	0	7.446593	-0.507558	1.670584
18	C	0	4.638563	-0.505796	0.378331
19	C	0	0.583506	-0.484180	-0.018554
20	C	0	-0.621786	-0.474576	-0.138492
21	C	0	-2.048567	-0.461287	-0.281615
22	C	0	-2.694849	0.578045	-0.963486
23	H	0	-2.106443	1.370924	-1.381366
24	C	0	-4.066794	0.594484	-1.103018
25	H	0	-4.565406	1.386828	-1.623741
26	C	0	-2.835254	-1.478420	0.251061
27	H	0	-2.360824	-2.283786	0.776552
28	C	0	-4.217863	-1.471114	0.115755
29	H	0	-4.789822	-2.271597	0.538740
30	C	0	-4.833818	-0.431660	-0.562682
31	C	0	-7.105567	-1.313575	-0.239952
32	H	0	-6.997227	-1.384757	0.837143
33	H	0	-6.876148	-2.280480	-0.673629
34	C	0	-8.507321	-0.871060	-0.618070
35	H	0	-8.556284	-0.777413	-1.697832
36	H	0	-9.199279	-1.661316	-0.334413
37	C	0	-8.929527	0.447164	0.038425
38	H	0	-8.226473	1.221875	-0.246097
39	H	0	-8.860407	0.341610	1.117912
40	C	0	-10.350337	0.868289	-0.357181
41	H	0	-10.412376	0.905254	-1.442396
42	H	0	-11.058804	0.106415	-0.036215
43	C	0	-10.786595	2.230140	0.204252
44	H	0	-11.738397	2.501014	-0.244930
45	H	0	-10.074442	2.989515	-0.108950
46	C	0	-10.932866	2.265347	1.729394
47	H	0	-11.310867	3.227198	2.058902
48	H	0	-9.985839	2.099460	2.229235
49	H	0	-11.627207	1.503338	2.070171
50	N	0	5.782622	-0.507600	0.487692
51	O	0	-6.192244	-0.333367	-0.751063

Mulliken atomic charge distribution for complex **1**

1	Au	0.726778	27	H	0.164158
2	C	-0.519124	28	C	-0.184493
3	H	0.177200	29	H	0.165275
4	H	0.184061	30	C	0.275433
5	H	0.177204	31	C	-0.110501
6	C	-0.348106	32	H	0.173063
7	H	0.180020	33	H	0.176024
8	H	0.180022	34	C	-0.354540
9	C	-0.332229	35	H	0.185727
10	H	0.175929	36	H	0.168911
11	H	0.175924	37	C	-0.325063
12	C	-0.355095	38	H	0.195561
13	H	0.200809	39	H	0.168402
14	H	0.200784	40	C	-0.335543
15	C	-0.131464	41	H	0.170030
16	H	0.233461	42	H	0.160715
17	H	0.233458	43	C	-0.350329
18	C	0.029368	44	H	0.170470
19	C	-0.076726	45	H	0.171531
20	C	-0.896723	46	C	-0.519014
21	C	0.033777	47	H	0.173503
22	C	-0.040170	48	H	0.179843
23	H	0.164223	49	H	0.169382
24	C	-0.193248	50	N	-0.451781
25	H	0.162244	51	O	-0.529386
26	C	-0.049755	Sum of Mulliken charges = 0.00000		

Table S3. Cartesian coordinates for complex **2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	Au	0	-0.176469	-0.364631	0.000177
2	C	0	8.976988	1.174770	-0.000350
3	H	0	9.295058	0.614553	-0.882976
4	H	0	9.295188	0.614389	0.882136
5	H	0	9.512667	2.125545	-0.000299
6	C	0	7.457553	1.395507	-0.000221
7	H	0	7.173959	1.987940	0.875868
8	H	0	7.173822	1.988069	-0.876182
9	C	0	6.659488	0.079775	-0.000251
10	H	0	6.943777	-0.512228	0.877337
11	H	0	6.943599	-0.512091	-0.877990
12	C	0	5.138203	0.301527	-0.000081
13	H	0	4.843634	0.880895	0.878404
14	H	0	4.843454	0.880953	-0.878466
15	C	0	4.372382	-1.033342	-0.000039
16	H	0	4.629856	-1.623878	-0.881202
17	H	0	4.630059	-1.623948	0.881013
18	C	0	1.794283	-0.663153	0.000232
19	C	0	-2.144255	-0.069464	0.000067
20	C	0	-3.354656	0.110352	-0.000042
21	C	0	-4.766798	0.320752	-0.000124
22	C	0	-5.304241	1.626241	0.000244
23	H	0	-4.626964	2.469067	0.000588
24	C	0	-6.683384	1.828647	0.000165
25	H	0	-7.076185	2.837309	0.000456
26	C	0	-7.558183	0.737781	-0.000281
27	H	0	-8.628404	0.897475	-0.000339
28	C	0	-7.040241	-0.561057	-0.000645
29	H	0	-7.710783	-1.410836	-0.000990
30	C	0	-5.662123	-0.770782	-0.000568
31	H	0	-5.260954	-1.774813	-0.000845
32	N	0	2.949886	-0.842552	0.000130

Mulliken atomic charge distribution for complex **2**

1	Au	0.798169	18	C	-0.013114
2	C	-0.515991	19	C	-0.096979
3	H	0.176113	20	C	-0.878990
4	H	0.176110	21	C	0.038749
5	H	0.182989	22	C	-0.057492
6	C	-0.345405	23	H	0.165362
7	H	0.178487	24	C	-0.166129
8	H	0.178486	25	H	0.144090
9	C	-0.329507	26	C	-0.134831
10	H	0.174418	27	H	0.145267
11	H	0.174419	28	C	-0.166211
12	C	-0.351214	29	H	0.144138
13	H	0.198829	30	C	-0.057301
14	H	0.198831	31	H	0.165735
15	C	-0.132188	32	N	-0.457654
16	H	0.231408	Sum of Mulliken charges = 0.00000		
17	H	0.231406			

Table S4. Cartesian coordinates for complex **3**.

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	Au	0	-1.241897	-0.515354	0.048689
2	C	0	-10.239195	1.621734	-0.176851
3	H	0	-10.619349	0.951837	-0.951897
4	H	0	-10.697099	2.600243	-0.330615
5	H	0	-10.582715	1.242467	0.788641
6	C	0	-8.707229	1.713245	-0.223942
7	H	0	-8.394038	2.125106	-1.188777
8	H	0	-8.358986	2.417791	0.538393
9	C	0	-8.017713	0.354337	-0.007643
10	H	0	-8.365066	-0.350314	-0.771868
11	H	0	-8.330549	-0.057281	0.958691
12	C	0	-6.483858	0.450955	-0.054314
13	H	0	-6.162978	0.852283	-1.018722
14	H	0	-6.129105	1.142644	0.713717
15	C	0	-5.821052	-0.921019	0.163113
16	H	0	-6.107556	-1.338289	1.129918
17	H	0	-6.132523	-1.626750	-0.608785
18	C	0	-3.225103	-0.723634	0.097245
19	C	0	0.737147	-0.292635	0.004969
20	C	0	1.952059	-0.150541	-0.017497
21	C	0	3.366124	0.018712	-0.039095
22	C	0	3.947997	1.280991	0.212254
23	H	0	3.303100	2.122319	0.420593
24	C	0	4.223591	-1.069128	-0.314773
25	H	0	3.791405	-2.039290	-0.512597
26	C	0	5.327703	1.446920	0.195182
27	H	0	5.759757	2.419266	0.382424
28	C	0	5.603654	-0.903705	-0.331573
29	H	0	6.248258	-1.742846	-0.549387
30	C	0	6.161229	0.356697	-0.083995
31	C	0	7.635707	0.520138	-0.032098
32	F	0	8.315456	-0.380119	-0.864681
33	F	0	8.165803	0.311306	1.257527
34	F	0	8.055989	1.805580	-0.403219
35	N	0	-4.387754	-0.836508	0.128758

Mulliken atomic charge distribution for complex **3**

1	Au	0.815572	19	C	-0.073103
2	C	-0.516075	20	C	-0.895429
3	H	0.176557	21	C	0.086422
4	H	0.183852	22	C	-0.074044
5	H	0.176521	23	H	0.176463
6	C	-0.345361	24	C	-0.075619
7	H	0.178819	25	H	0.176817
8	H	0.178831	26	C	-0.091918
9	C	-0.329748	27	H	0.181675
10	H	0.175166	28	C	-0.092000
11	H	0.175224	29	H	0.181929
12	C	-0.351771	30	C	-0.171405
13	H	0.199323	31	C	0.751383
14	H	0.199464	32	F	-0.290033
15	C	-0.134036	33	F	-0.282356
16	H	0.233452	34	F	-0.289995
17	H	0.233215	35	N	-0.453390
18	C	-0.014402	Sum of Mulliken charges = 0.00000		

Table S5. Cartesian coordinates for complex **4**.

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	Au	0	-1.842686	-0.473226	-0.017438
2	C	0	-10.953776	1.325510	0.039928
3	H	0	-11.292429	0.773482	-0.840176
4	H	0	-11.464743	2.289686	0.043344
5	H	0	-11.279994	0.773850	0.924936
6	C	0	-9.429254	1.507199	0.029086
7	H	0	-9.136574	2.092364	-0.848863
8	H	0	-9.123996	2.091604	0.903244
9	C	0	-8.666350	0.170724	0.022974
10	H	0	-8.972168	-0.412740	-0.853031
11	H	0	-8.960083	-0.413923	0.902309
12	C	0	-7.139640	0.352461	0.012639
13	H	0	-6.836016	0.924954	-0.867241
14	H	0	-6.823862	0.922224	0.890010
15	C	0	-6.411615	-1.003304	0.005466
16	H	0	-6.677951	-1.588441	0.887351
17	H	0	-6.689065	-1.585099	-0.875194
18	C	0	-3.824112	-0.707634	-0.009198
19	C	0	0.138356	-0.248004	-0.023445
20	C	0	1.353959	-0.116620	-0.025271
21	C	0	2.769639	0.032229	-0.025409
22	C	0	3.363143	1.311616	-0.037633
23	H	0	2.729969	2.185544	-0.052561
24	C	0	3.615316	-1.093760	-0.018044
25	H	0	3.177385	-2.080731	-0.017020
26	C	0	4.750121	1.448432	-0.049587
27	C	0	5.002572	-0.939500	-0.026942
28	C	0	5.584912	0.327903	-0.034249
29	N	0	-4.983017	-0.852570	-0.003143
30	H	0	6.656906	0.440118	-0.051206
31	C	0	5.356225	2.809809	0.001055
32	C	0	5.860260	-2.158566	0.021283
33	F	0	5.832775	-2.782426	1.279177
34	F	0	5.450952	-3.138214	-0.893660
35	F	0	7.203790	-1.888546	-0.252349
36	F	0	6.619937	2.858128	-0.598261
37	F	0	5.537556	3.267292	1.317292
38	F	0	4.569142	3.775874	-0.634667

Mulliken atomic charge distribution for complex **4**

1	Au	0.827340	21	C	0.085194
2	C	-0.515955	22	C	0.008223
3	H	0.176754	23	H	0.210593
4	H	0.184296	24	C	0.017977
5	H	0.176796	25	H	0.207690
6	C	-0.345740	26	C	-0.201384
7	H	0.179047	27	C	-0.201000
8	H	0.179071	28	C	-0.026869
9	C	-0.329835	29	N	-0.451033
10	H	0.175563	30	H	0.220454
11	H	0.175620	31	C	0.766934
12	C	-0.351792	32	C	0.769724
13	H	0.199628	33	F	-0.276267
14	H	0.199691	34	F	-0.280943
15	C	-0.134592	35	F	-0.284869
16	H	0.234802	36	F	-0.283086
17	H	0.234733	37	F	-0.274795
18	C	-0.015895	38	F	-0.282584
19	C	-0.045297	Sum of Mulliken charges = 0.00000		
20	C	-0.928197			