Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Synergistic Luminescence Enhancement of a Pyridyl-substituted Triarylmethyl Radical Based on Fluorine Substitution and Coordination to Gold

Yohei Hattori,[a] Tetsuro Kusamoto,*[a] Tohru Sato,[b] and Hiroshi Nishihara*[a]

[a]Department of Chemistry, School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[b]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Nishikyo-ku, Kyoto, 615-8510, Japan.

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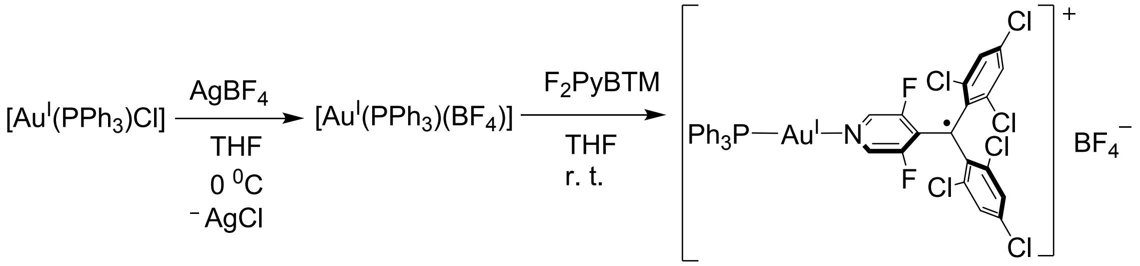
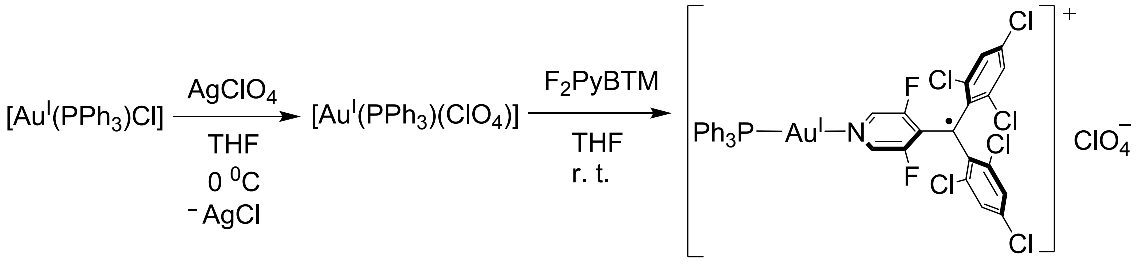
Synthesis of $[Au^I(F_2PyBTM)PPh_3]BF_4$



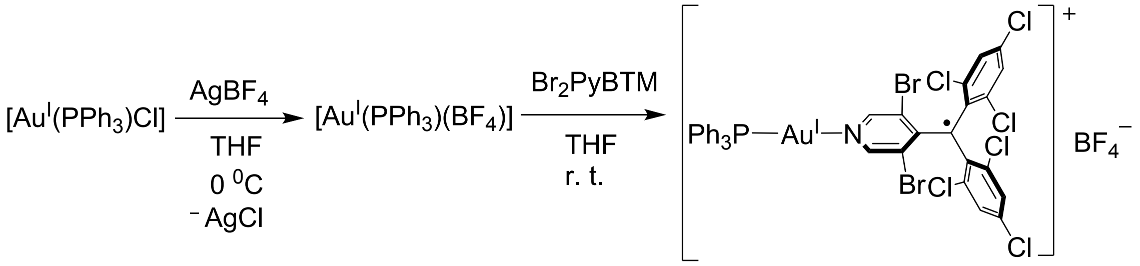
$[Au^I(F_2PyBTM)PPh_3]BF_4$ was synthesized by similar method to $[Au^I(PyBTM)PPh_3]BF_4$ utilizing modified literature procedure.[1] Under an nitrogen atmosphere, chloro(triphenylphosphine)gold(I) (24.9 mg, 0.0503 mmol) was dissolved in dry THF (2 mL) and silver tetrafluoroborate (ca. 20 mg, 0.1 mmol) was added at 0°C, stirred for 15 min, and filtered. The filtrate was added to a solution of F_2PyBTM (25.0 mg, 0.0513 mmol) in THF (2 mL), and stirred at room temperature for 30 min, and then evaporated. Red powder was precipitated from dichloromethane -diethyl ether (−30 °C), washed with diethyl ether, and dried in vacuo to afford $[Au^I(PyBTM)PPh_3]BF_4$ (25.8 mg, 0.0250 mmol, 50% yield). **ESI-TOF-MS** m/z: $[Au^I(F_2PyBTM)PPh_3]^+$ Calcd for $C_{36}H_{21}NAuCl_6F_2P$ 974.9177; Found 974.9055.

Synthesis of $[Au^I(F_2PyBTM)PPh_3]ClO_4$



$[Au^I(F_2PyBTM)PPh_3]ClO_4$ was synthesized by a similar method to $[Au^I(PyBTM)PPh_3]ClO_4$ according to the literature procedure.[1] Under an nitrogen atmosphere, chloro(triphenylphosphine)gold(I) (7.4 mg, 0.015 mmol) was dissolved in dry THF (2 mL) and silver perchlorate (**Caution: perchlorate salts are potentially explosive**, 5 mg, 0.025 mmol) was added at 0°C, stirred for 15 min, and filtered. The filtrate was added to a solution of F_2PyBTM (7.5 mg, 0.015 mmol) in THF (2 mL), and stirred at room temperature for 30 min, and then evaporated. Red powder was precipitated from dichloromethane-hexane to afford $[Au^I(PyBTM)PPh_3]ClO_4$ (12.6 mg, 0.012 mmol, 80% yield).

Synthesis of $[Au^I(Br_2PyBTM)PPh_3]BF_4$



$[Au^I(Br_2PyBTM)PPh_3]BF_4$ was synthesized by a similar method to $[Au^I(PyBTM)PPh_3]BF_4$ utilizing modified literature procedure.[1] Under an nitrogen atmosphere, chloro(triphenylphosphine)gold(I) (25.5 mg, 0.0515 mmol) was dissolved in dry THF (2 mL) and silver tetrafluoroborate (ca. 20 mg, 0.1 mmol) was added at 0°C, stirred for 15 min, and filtered. The filtrate was added to a solution of Br_2PyBTM (32.5 mg, 0.0534 mmol) in THF (2 mL), and stirred at room temperature for 30 min, and then evaporated. Red powder was precipitated from dichloromethane -diethyl ether (−30 °C), washed with diethyl ether, and dried in vacuo to afford [Au^{I}(PyBTM)PPh$_3$]BF$_4$ (9.2 mg, 0.00797 mmol, 15% yield). **ESI-TOF-MS** m/z: [Au^{I}(Br$_2$PyBTM)PPh$_3$]$^+$ Calcd for $C_{36}H_{21}NAuBr_2Cl_6P$ 1062.7576; Found 1062.7595.

X-ray structural analysis

Red single crystals of [Au^{I}(F$_2$PyBTM)PPh$_3$]ClO$_4$ were obtained by diffusing hexane into a dichloromethane solution. Diffraction data for X-ray analysis were collected with an AFC10 diffractometer coupled with a Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated MoKα radiation (λ = 0.7107 Å). Lorentz polarization and numerical absorption corrections were performed with the program *Crystal Clear 1.3.6.* Structures were solved by the direct method using SIR 92 software[2] and refined against F^2 using SHELXL-97.[3] *Crystal Structure 4.0* software was used to prepare the material for publication. The crystallographic data are listed in Table 5-3. CCDC 1494043 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Instruments

ESR spectra were recorded with a JEOL JES-FA200 spectrometer with X-band microwave. Deoxygenated sample solutions were charged in a 5mmϕ sample tube. Magnetic field was calibrated with the Mn^{2+}/MgO standard. ESI–TOF mass spectra were recorded using an LCT Micromass spectrometer. UV-vis absorption spectra were recorded with a JASCO V-570 spectrometer. Steady-state emission spectra were measured with a HITACHI F-4500 spectrometer. Sample solutions were bubbled with argon before the measurements. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics C9920-02G. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics Quantaurus-Tau C11367-02.

Evaluation of stability under UV light

A 2mL solution and small stir bar in 1-cm-optical-path-length quartz cells were sealed, set at a JASCO FP-8600 spectrofluorometer, and stirred using mini-magnetic stirrer. Intensity of luminescence was observed exciting at 370 nm light (excitation slit was 5.0 nm, and shutter control was off). Radiation flux of a Xe lamp in fluorometer was measured using a photon counter (8230E, ADC Corporation). A JASCO FP-8600 spectrofluorometer can irradiate much stronger excitation light (~1200 μW) than a HITACHI F-4500 spectometer (~70 μW). Differences between previous evaluation and results reported here are attributed to the strength of excitation light.

Computational details

DFT calculations were executed using the Gaussian09 program package.[4] The geometries of the compounds were optimized without symmetry constraints using the crystal structure coordinate as the starting structure. Calculations were performed using M06 functional[5] with the SDD basis set (Au) and the 6-31G(d) basis set (H, C, N, P, Cl). Cartesian coordinates of all the optimized geometries are listed in the supporting information. Frequency calculations were carried out to ensure that the optimized geometries were minima on the potential energy surface, in which no imaginary frequencies were observed in any of the compounds. TD-DFT calculations were performed using M06 to calculate the first 15 doublet transitions.

References

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Table S1. Crystallographic data of $[\mathrm{Au^{I}(F_2PyBTM)PPh_3}]\mathrm{ClO_4}\cdot0.5$hexane

	$[\mathrm{Au^{I}(F_2PyBTM)PPh_3}]\cdot\mathrm{ClO_4}\cdot0.5$hexane
Empirical formula	$C_{39}H_{21}AuCl_9F_2NO_4P$
Fw / g mol^{-1}	1081.71
Crystal system	monoclinic
Space group	$P2_1/n$
Crystal size / mm	0.1 × 0.05 × 0.05
Temperature / K	113(2)
a / Å	8.7297(6)
b / Å	28.911(2)
c / Å	15.5735(12)
α / °	90
β / °	103.822(4)
γ / °	90
V / Å^3	3816.7(5)
Z	4
ρ_{calced} / g cm^{-3}	1.882
λ / Å	0.7107
μ / mm^{-1}	4.453
Reflections collected	30181
Independent reflections	8723
Parameters	481
R_{int}	0.0471
$^{a}R1$	0.0532
$^{b}wR2$	0.1221
^{c}GoF	1.080
CCDC No.	1494043

$^{a}R_1 = \Sigma||F^{o}|-|F^{c}||/\Sigma|F^{o}|$ $(I>2\sigma(I))$. $^{b}wR_2 = [\Sigma(w(F^{o2}-F^{c2})^2/\Sigma w(F^{o2})^2]^{1/2}$ $(I>2\sigma(I))$. $^{c}\mathrm{GOF} = [\Sigma(w(F^{o2}-F^{c2})^2/\Sigma(N^{r}-N^{p})^2]$.

Table S2. Summary of absorption and emission

	λ_{abs} [nm] (ε [10^3 M^{-1} cm^{-1}])	λ_{em} [nm]
[Au^I(F_2PyBTM)PPh_3]BF_4	367 (12), 419 (6.1), 557 (1.1)	622
[Au^I(PyBTM)PPh_3]BF_4	380 (23), 434 (11), 566 (1.9)	653
[Au^I(Br_2PyBTM)PPh_3]BF_4	381 (15), 438 (7.6), 571 (1.4)	666
F_2PyBTM	351 (16), 523 (0.85)	566
PyBTM	370 (25), 541 (1.0)	585
Br_2PyBTM	376 (20), 548 (1.0)	593

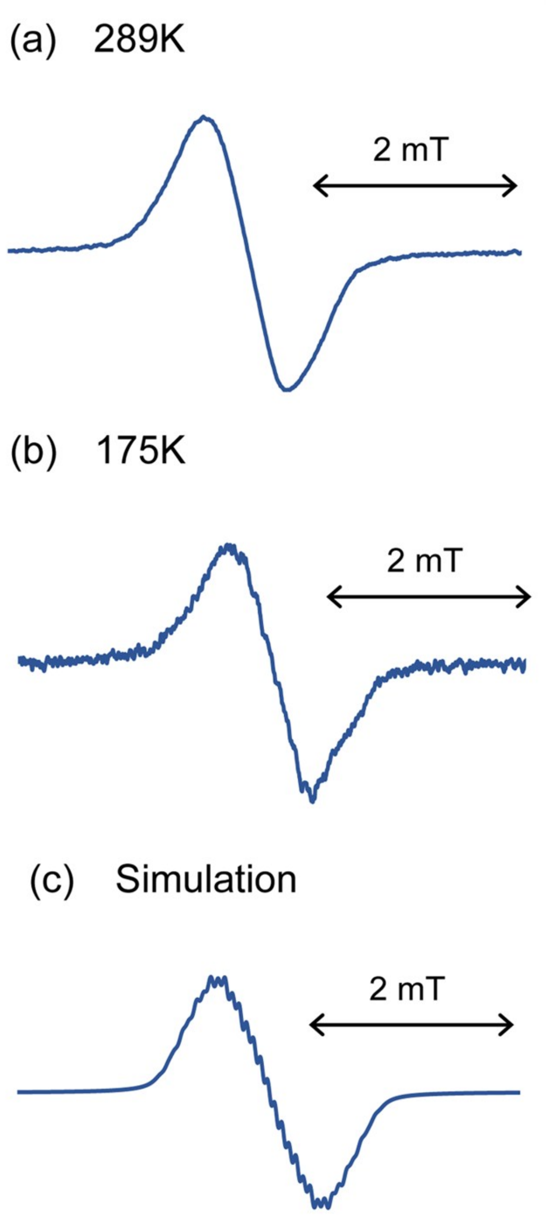

Fig. S1 ESR spectrum of [Au^{I}(F$_2$PyBTM)PPh$_3$]BF$_4$ at (a) 289K, (b) 175 K in dichloromethane. (c) Simulated ESR spectrum using calculated hyperfine coupling constants (0.35 mT with ^{14}N, 0.29 mT with 2^{19}F, 0.14 mT with ^{31}P, 0.15 mT with 2^{1}H, 0.13 mT with 2^{1}H, and 0.08 mT with 2^{1}H).

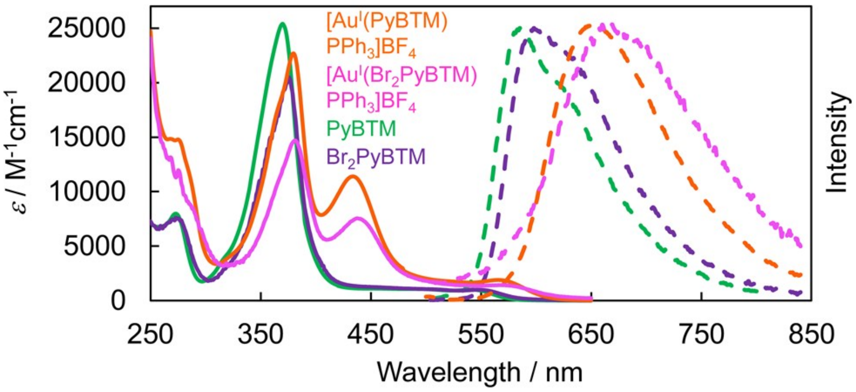

Fig. S2 Absorption and emission spectra of [Au^I(Br$_2$PyBTM)PPh$_3$]BF$_4$ (pink line), [Au^I(PyBTM)PPh$_3$]BF$_4$ (orange line), Br$_2$PyBTM (purple line) and PyBTM (green line) in dichloromethane.

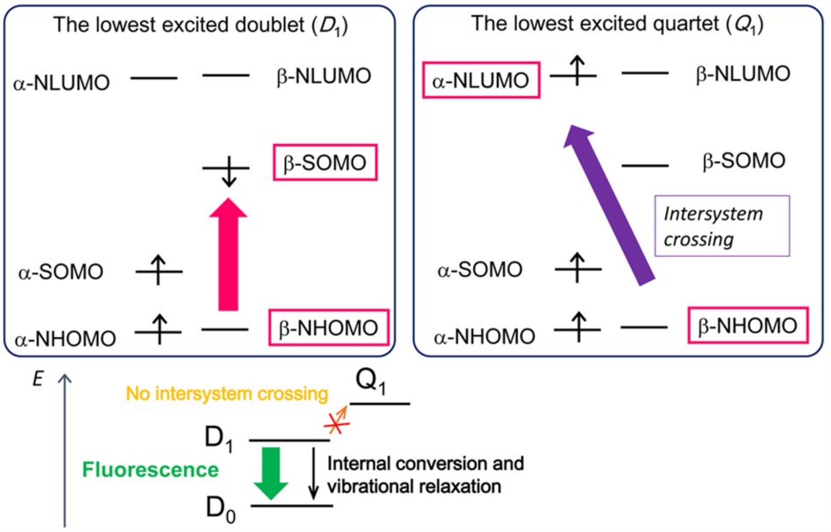

Fig. S3 Comparison between D$_1$ and Q$_1$ states. The D$_1$ state is lower in energy than the Q$_1$ state and D$_1$→Q$_1$ intersystem crossing does not occur.

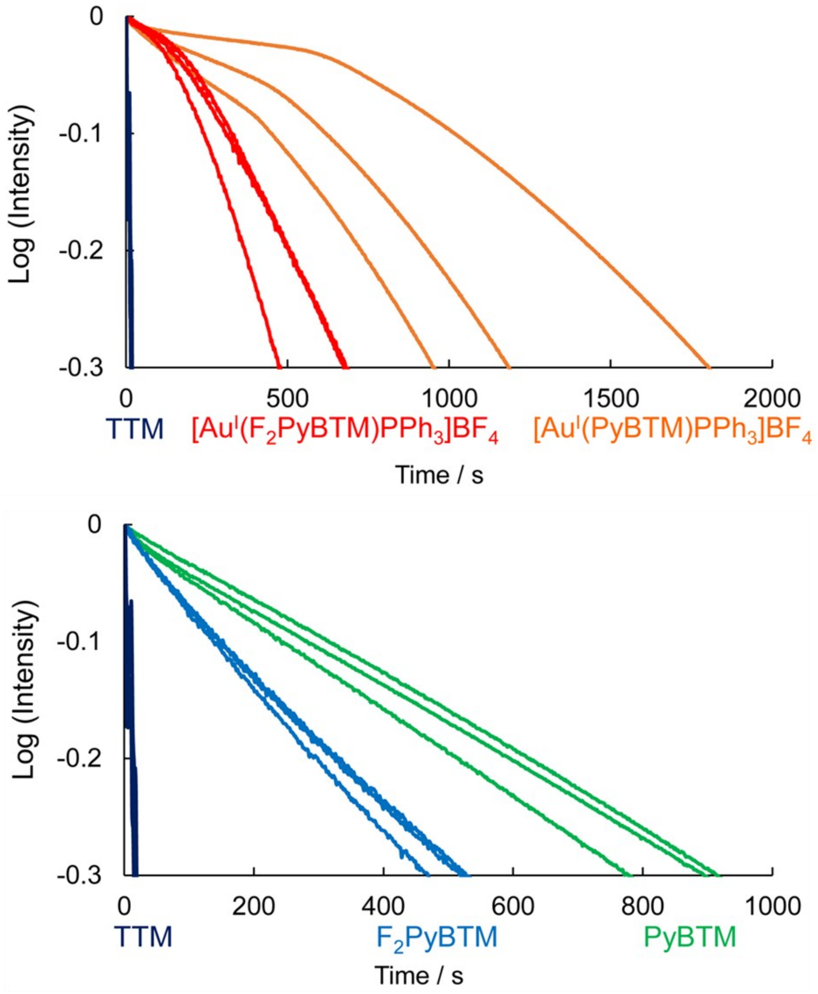

Fig. S4 Plots showing the emission decay of [Au^I(F$_2$PyBTM)PPh$_3$]BF$_4$ (3 red lines), [Au^I(PyBTM)PPh$_3$]BF$_4$ (3 orange lines), F$_2$PyBTM (3 blue lines), PyBTM (3 green lines), and TTM (3 deep blue lines) in dichloromethane under continuous excitation with light at λ_{ex} = 370 nm. The half-lives ([Au^I(F$_2$PyBTM)PPh$_3$]BF$_4$: $t_{1/2}$ = 600 ± 100 s, [Au^I(PyBTM)PPh$_3$]BF$_4$: $t_{1/2}$ = 1300 ± 400 s, F$_2$PyBTM: $t_{1/2}$ = 500 ± 100 s, PyBTM: $t_{1/2}$ = 900 ± 100 s) were estimated. Note that the photostability of PyBTM derivatives is much higher than that of TTM ($t_{1/2}$ = 17 ± 3 s). Multiplication of the absorption coefficients at 370 nm (A_{370}) and the half-lives ($t_{1/2}$) equals to (7 ± 1) × 10^6 s M^{-1} cm^{-1} for [Au^I(F$_2$PyBTM)PPh$_3$]BF$_4$, (2.5 ± 0.8) × 10^7 s M^{-1} cm^{-1} for [Au^I(PyBTM)PPh$_3$]BF$_4$, (6 ± 1) × 10^6 s M^{-1} cm^{-1} for F$_2$PyBTM, (2.3 ± 0.3) × 10^7 s M^{-1} cm^{-1} for PyBTM, and (3 ± 1) × 10^5 s M^{-1} cm^{-1} for TTM.

A JASCO FP-8600 spectrofluorometer used for the present study irradiates much stronger excitation light (~1200 µW) than a HITACHI F-4500 spectometer (~70 µW) used for our previous studies does. Differences in $t_{1/2}$ between previous reports and present study are attributed to the strength of excitation light. While PyBTM and F$_2$PyBTM showed exponential decay, gold complexes displayed slightly accelerated decay probably because of multi-step process. Gold complexes showed slower decomposition than ligands do at shorter irradiation time (Log (intensity) > −0.05).

Cartesian coordinates of all the optimized geometries by DFT calculation

UM06/ SDD(Au), 6-31G(d)(H, C, N, F, P, Cl)

```
                         Standard orientation:
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         79           0        2.622986   -0.018801    0.069232
      2         17           0       -5.995178    0.236270    2.191286
      3         17           0       -6.906787    5.145140    0.274688
      4         17           0       -5.915628   -0.202004   -2.232172
      5         17           0       -6.976445   -5.098286   -0.362156
      6         17           0       -3.123552   -2.261474    2.027503
      7         17           0       -3.011756    2.243288   -1.962438
      8         15           0        4.939470   -0.004097   -0.001815
      9          7           0        0.481132   -0.031021    0.087543
     10          6           0       -6.321598    2.636255    1.082846
     11          6           0       -2.358216   -0.014171    0.046873
     12          6           0       -1.587120    0.921166    0.764985
     13          6           0       -0.208207    0.895984    0.774825
     14          6           0       -0.199480   -0.952286   -0.616457
     15          6           0       -1.578218   -0.961649   -0.645214
     16          6           0       -3.799491   -0.001920    0.020693
     17          6           0       -4.545121   -1.258376   -0.100596
     18          6           0       -4.310481   -2.360448    0.750220
     19          6           0       -5.574937   -1.432281   -1.049857
     20          6           0       -6.322175   -2.597291   -1.141028
     21          6           0       -6.050213   -3.640269   -0.266400
     22          6           0       -5.042290   -3.533178    0.685199
     23          6           0       -4.527806    1.267166    0.112930
     24          6           0       -5.589938    1.459373    1.022199
     25          6           0       -6.000115    3.672840    0.217373
     26          6           0       -4.958351    3.547896   -0.694732
     27          6           0       -4.243215    2.363649   -0.729727
     28          6           0        5.695752   -0.581892    1.541641
     29          6           0        5.135541   -1.678372    2.206136
     30          6           0        5.741934   -2.178042    3.351758
     31          6           0        6.902693   -1.582228    3.840078
     32          6           0        7.461243   -0.490908    3.181901
     33          6           0        6.862522    0.011386    2.031260
     34          6           0        5.593470    1.659869   -0.311710
```

35	6	0	5.057311	2.734626	0.406293
36	6	0	5.580140	4.010223	0.239851
37	6	0	5.562006	-1.069649	-1.332231
38	6	0	6.642652	-1.931125	-1.130629
39	6	0	7.119974	-2.697345	-2.190086
40	6	0	6.527681	-2.601163	-3.444956
41	6	0	5.452917	-1.738014	-3.649779
42	6	0	4.966632	-0.976255	-2.595798
43	6	0	6.653500	1.870004	-1.196972
44	6	0	6.633930	4.218382	-0.647607
45	6	0	7.168732	3.152000	-1.363260
46	1	0	-7.123497	2.745583	1.808032
47	1	0	0.343674	1.632238	1.353227
48	1	0	0.359991	-1.695659	-1.178433
49	1	0	-7.097289	-2.692738	-1.896703
50	1	0	-4.843771	-4.345909	1.378569
51	1	0	-4.720930	4.355690	-1.381662
52	1	0	4.225651	-2.143671	1.822495
53	1	0	5.305447	-3.030237	3.868427
54	1	0	7.372772	-1.970704	4.741280
55	1	0	8.367360	-0.026617	3.565403
56	1	0	7.303218	0.864865	1.516358
57	1	0	4.233646	2.569033	1.103426
58	1	0	5.163080	4.845015	0.799252
59	1	0	7.111084	-2.005969	-0.149566
60	1	0	7.959178	-3.371570	-2.032328
61	1	0	6.903983	-3.202862	-4.269833
62	1	0	4.991205	-1.662641	-4.632089
63	1	0	4.126459	-0.297348	-2.755221
64	1	0	7.077114	1.035515	-1.755492
65	1	0	7.039188	5.219245	-0.781990
66	1	0	7.992128	3.316550	-2.055128
67	9	0	-2.188056	1.854375	1.483146
68	9	0	-2.169351	-1.888549	-1.379494

Extracted results of TD-DFT calculation.

UM06/ SDD(Au), 6-31G(d)(H, C, N, F, P, Cl)

Excitation energies and oscillator strengths:

```
 Excited State   1:   2.104-A      2.2489 eV   551.30 nm   f=0.0489   <S**2>=0.857
      199A ->205A        -0.11371
      186B ->199B        -0.10980
      196B ->199B        -0.12890
      198B ->199B         0.95099
      198B ->200B        -0.11937
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =   -4875.52523126
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:   2.101-A      2.3638 eV   524.51 nm   f=0.0104   <S**2>=0.853
      199A ->200A        -0.11949
      194B ->199B         0.35311
      197B ->199B         0.89956

 Excited State   3:   2.080-A      2.4713 eV   501.69 nm   f=0.0070   <S**2>=0.831
      196B ->199B         0.97111
      198B ->199B         0.15485

 Excited State   4:   2.116-A      2.4974 eV   496.46 nm   f=0.0302   <S**2>=0.869
      199A ->200A        -0.19843
      187B ->199B         0.10794
      194B ->199B         0.85076
      197B ->199B        -0.40440

 Excited State   5:   2.157-A      2.8980 eV   427.83 nm   f=0.2367   <S**2>=0.913
      192A ->200A         0.14746
      199A ->200A         0.85822
      182B ->199B        -0.14310
      187B ->199B        -0.24879
      194B ->199B         0.27834

 Excited State   6:   2.117-A      3.0885 eV   401.44 nm   f=0.0005   <S**2>=0.871
      195B ->199B         0.99157

 Excited State   7:   2.381-A      3.1403 eV   394.81 nm   f=0.0058   <S**2>=1.168
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      199A ->204A        -0.20140
      186B ->199B         0.15746
      188B ->199B         0.90336
      188B ->200B         0.14763

 Excited State   8:    3.115-A      3.2768 eV   378.37 nm   f=0.0558   <S**2>=2.175
      196A ->210A        -0.24411
      197A ->205A        -0.10157
      197A ->209A         0.26435
      198A ->200A        -0.24274
      198A ->214A         0.14416
      198A ->217A         0.10948
      199A ->204A        -0.26197
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      199A ->209A         0.10812
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      194B ->205B        -0.12698
      194B ->209B         0.11453
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      196B ->211B         0.22129
      197B ->205B        -0.10875
      197B ->209B        -0.20790
      198B ->199B         0.21157
      198B ->200B         0.25268
      198B ->217B         0.14192

 Excited State   9:    3.011-A      3.3138 eV   374.14 nm   f=0.0619   <S**2>=2.016
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      196A ->205A         0.15733
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      197A ->210A         0.20953
      198A ->204A         0.12922
      198A ->205A        -0.20623
      198A ->209A        -0.12177
      199A ->200A         0.12861
      199A ->214A        -0.17846
      199A ->217A        -0.11940
      173B ->199B         0.10506
      182B ->199B         0.19424
      187B ->199B         0.53549
      188B ->204B         0.10030
      194B ->199B         0.10729
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     194B ->200B         0.21090
     194B ->217B         0.10203
     196B ->205B         0.11353
     196B ->209B         0.15986
     197B ->211B        -0.19761
     198B ->204B        -0.16278
     198B ->205B        -0.12342
     198B ->209B         0.12525

 Excited State  10:    2.221-A      3.4497 eV  359.40 nm  f=0.0000  <S**2>=0.984
     192B ->199B        -0.40566
     193B ->199B         0.87517

 Excited State  11:    2.274-A      3.4537 eV  358.99 nm  f=0.0004  <S**2>=1.042
     192B ->199B         0.84459
     193B ->199B         0.43084

 Excited State  12:    3.441-A      3.4648 eV  357.84 nm  f=0.0000  <S**2>=2.710
     189A ->203A        -0.16529
     189A ->208A        -0.13303
     190A ->201A         0.10945
     190A ->202A         0.16298
     190A ->203A        -0.12344
     190A ->207A        -0.14899
     190A ->208A        -0.12407
     191A ->206A         0.13405
     191A ->211A        -0.17333
     193A ->207A         0.11556
     193A ->212A        -0.17378
     193A ->213A        -0.17062
     194A ->208A        -0.10462
     195A ->201A         0.27614
     195A ->206A        -0.11480
     195A ->211A        -0.10678
     189B ->203B         0.17421
     189B ->208B         0.13963
     190B ->201B        -0.11485
     190B ->202B        -0.16405
     190B ->203B         0.10475
     190B ->206B        -0.10446
     190B ->207B         0.10798
     190B ->208B         0.10702
     191B ->210B         0.17286
```

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      192B ->199B        -0.17625
      192B ->207B        -0.10369
      192B ->212B         0.17216
      192B ->213B         0.17306
      193B ->208B         0.10120
      195B ->201B        -0.27753
      195B ->205B         0.11132
      195B ->207B         0.11632
      195B ->210B         0.10892
      195B ->214B         0.10373

 Excited State  13:   3.375-A      3.4768 eV  356.61 nm  f=0.0000  <S**2>=2.598
      189A ->201A         0.16595
      189A ->203A         0.14185
      189A ->208A         0.12364
      190A ->201A         0.10855
      190A ->207A        -0.11206
      190A ->211A        -0.10154
      191A ->212A        -0.19550
      193A ->206A         0.13193
      193A ->211A        -0.16378
      193A ->213A        -0.12048
      194A ->201A         0.10267
      194A ->212A        -0.14731
      195A ->203A        -0.25678
      195A ->208A        -0.21135
      189B ->201B        -0.17416
      189B ->203B        -0.14253
      189B ->208B        -0.11826
      191B ->212B         0.19590
      192B ->199B         0.29041
      192B ->210B         0.16199
      192B ->213B         0.12321
      193B ->201B        -0.10462
      193B ->212B         0.15049
      195B ->203B         0.25362
      195B ->208B         0.20612

 Excited State  14:   3.430-A      3.4819 eV  356.09 nm  f=0.0000  <S**2>=2.690
      189A ->202A        -0.16895
      189A ->207A         0.15930
      190A ->201A        -0.12889
      190A ->202A         0.10983
```

```
      190A ->203A        0.11294
      190A ->207A       -0.11607
      191A ->213A        0.17458
      194A ->206A       -0.12489
      194A ->211A        0.17776
      194A ->212A        0.10417
      194A ->213A       -0.19432
      195A ->202A       -0.23485
      195A ->207A        0.21678
      189B ->202B        0.16126
      189B ->206B        0.11069
      189B ->207B       -0.10284
      190B ->201B        0.13005
      190B ->202B       -0.12657
      190B ->203B       -0.12006
      190B ->206B       -0.13768
      191B ->213B       -0.17543
      193B ->199B        0.20248
      193B ->210B       -0.17646
      193B ->213B        0.19546
      195B ->202B        0.23555
      195B ->206B        0.17838
      195B ->207B       -0.13255

 Excited State  15:   2.771-A     3.5987 eV  344.52 nm  f=0.1116  <S**2>=1.670
      196A ->205A       -0.11495
      196A ->209A        0.23374
      197A ->210A       -0.26179
      198A ->205A        0.11727
      198A ->209A        0.13642
      199A ->200A        0.37611
      182B ->199B        0.11806
      187B ->199B        0.57090
      188B ->204B        0.10184
      189B ->199B        0.11358
      194B ->199B       -0.13976
      194B ->200B       -0.13299
      196B ->209B       -0.21775
      197B ->211B        0.24475
      198B ->204B        0.13128
      198B ->209B       -0.12825
```

Calculated hyperfine coupling constants

UM06/ SDD(Au), 6-31G(d)(H, C, N, F, P, Cl)

Isotropic Fermi Contact Couplings

	Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1
1	Au(197	0.00000	-0.00001	0.00000	0.00000
2	Cl(35)	0.00117	0.51096	0.18232	0.17044
3	Cl(35)	0.00255	1.11995	0.39963	0.37358
4	Cl(35)	0.00109	0.47820	0.17063	0.15951
5	Cl(35)	0.00257	1.12485	0.40137	0.37521
6	Cl(35)	0.00200	0.87581	0.31251	0.29214
7	Cl(35)	0.00202	0.88704	0.31652	0.29589
8	P(31)	-0.00217	-3.93466	-1.40399	-1.31246
9	N(14)	0.03028	9.78228	3.49056	3.26302
10	C(13)	-0.00723	-8.12914	-2.90068	-2.71159
11	C(13)	-0.03469	-39.00356	-13.91744	-13.01019
12	C(13)	0.02241	25.19566	8.99044	8.40437
13	C(13)	-0.01015	-11.40646	-4.07011	-3.80478
14	C(13)	-0.01010	-11.35951	-4.05336	-3.78912
15	C(13)	0.02250	25.29643	9.02640	8.43798
16	C(13)	0.09807	110.24481	39.33809	36.77371
17	C(13)	-0.03276	-36.83125	-13.14231	-12.28558
18	C(13)	0.02789	31.34900	11.18610	10.45690
19	C(13)	0.02724	30.62008	10.92600	10.21376
20	C(13)	-0.00726	-8.15989	-2.91165	-2.72185
21	C(13)	0.01288	14.47843	5.16626	4.82948
22	C(13)	-0.00721	-8.10571	-2.89232	-2.70377
23	C(13)	-0.03273	-36.79005	-13.12760	-12.27184
24	C(13)	0.02724	30.62005	10.92599	10.21375
25	C(13)	0.01283	14.42881	5.14856	4.81293
26	C(13)	-0.00718	-8.07072	-2.87983	-2.69210
27	C(13)	0.02786	31.31848	11.17521	10.44672
28	C(13)	0.00014	0.15585	0.05561	0.05199
29	C(13)	0.00002	0.02446	0.00873	0.00816
30	C(13)	0.00000	0.00433	0.00155	0.00144
31	C(13)	0.00000	-0.00102	-0.00036	-0.00034
32	C(13)	0.00001	0.01089	0.00389	0.00363
33	C(13)	-0.00001	-0.01619	-0.00578	-0.00540
34	C(13)	0.00009	0.09818	0.03503	0.03275
35	C(13)	0.00000	-0.00184	-0.00066	-0.00061
36	C(13)	0.00000	0.00272	0.00097	0.00091
37	C(13)	-0.00002	-0.02789	-0.00995	-0.00930

38	C(13)	-0.00003	-0.03109	-0.01109	-0.01037
39	C(13)	0.00000	-0.00016	-0.00006	-0.00005
40	C(13)	-0.00001	-0.00818	-0.00292	-0.00273
41	C(13)	0.00001	0.01034	0.00369	0.00345
42	C(13)	0.00001	0.00811	0.00289	0.00270
43	C(13)	-0.00002	-0.02215	-0.00790	-0.00739
44	C(13)	0.00000	-0.00149	-0.00053	-0.00050
45	C(13)	0.00000	0.00547	0.00195	0.00182
46	H(1)	0.00093	4.17004	1.48797	1.39097
47	H(1)	0.00051	2.27988	0.81352	0.76049
48	H(1)	0.00049	2.19992	0.78499	0.73381
49	H(1)	0.00093	4.17525	1.48983	1.39271
50	H(1)	0.00080	3.57811	1.27676	1.19353
51	H(1)	0.00080	3.57498	1.27564	1.19248
52	H(1)	0.00000	-0.01271	-0.00454	-0.00424
53	H(1)	0.00000	0.00573	0.00204	0.00191
54	H(1)	0.00000	0.00119	0.00043	0.00040
55	H(1)	0.00000	-0.00174	-0.00062	-0.00058
56	H(1)	0.00000	0.00887	0.00316	0.00296
57	H(1)	0.00000	-0.00429	-0.00153	-0.00143
58	H(1)	0.00000	0.00306	0.00109	0.00102
59	H(1)	0.00000	0.00243	0.00087	0.00081
60	H(1)	0.00000	-0.00628	-0.00224	-0.00209
61	H(1)	0.00000	0.00513	0.00183	0.00171
62	H(1)	0.00000	-0.00089	-0.00032	-0.00030
63	H(1)	0.00000	0.00270	0.00096	0.00090
64	H(1)	0.00000	0.00765	0.00273	0.00255
65	H(1)	0.00000	0.00060	0.00021	0.00020
66	H(1)	0.00000	-0.00281	-0.00100	-0.00094
67	F(19)	0.00194	8.17147	2.91578	2.72571
68	F(19)	0.00193	8.10739	2.89292	2.70434