Effect of Gold(I) Coordination on the Dual Fluorescence of 4-(Dimethylamino)pyridine

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ELECTRONIC SUPPLEMENTARY INFORMATION

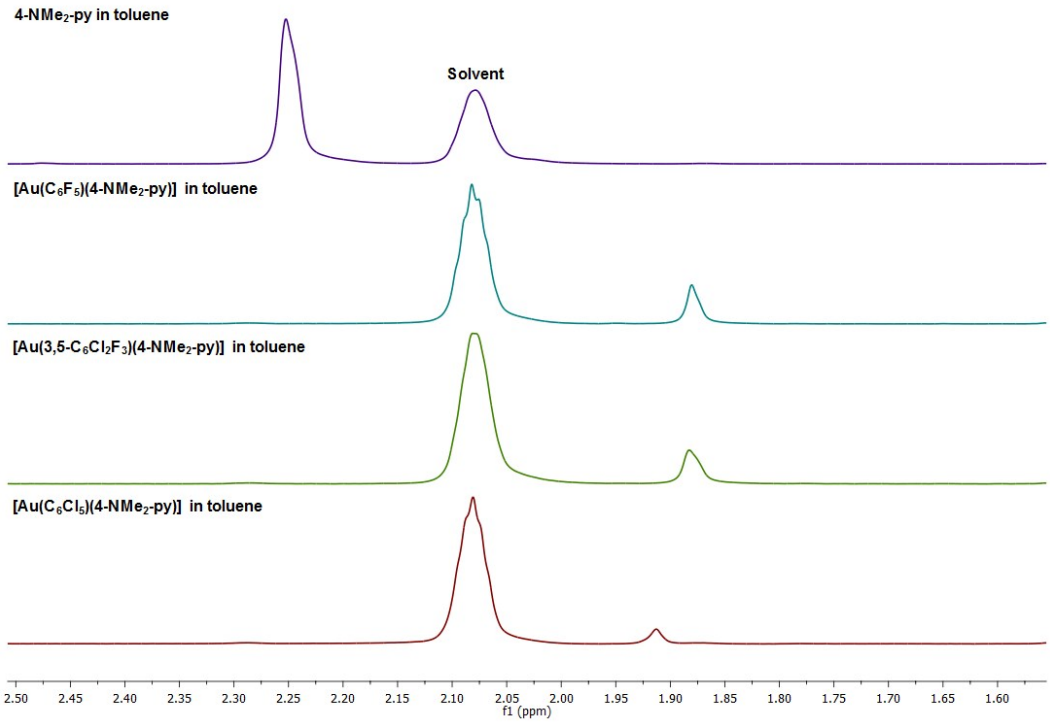


Figure S1. ^{1}H NMR spectra of complexes **1-3** and free DMAP in d8-toluene for the –NMe_2 signals.

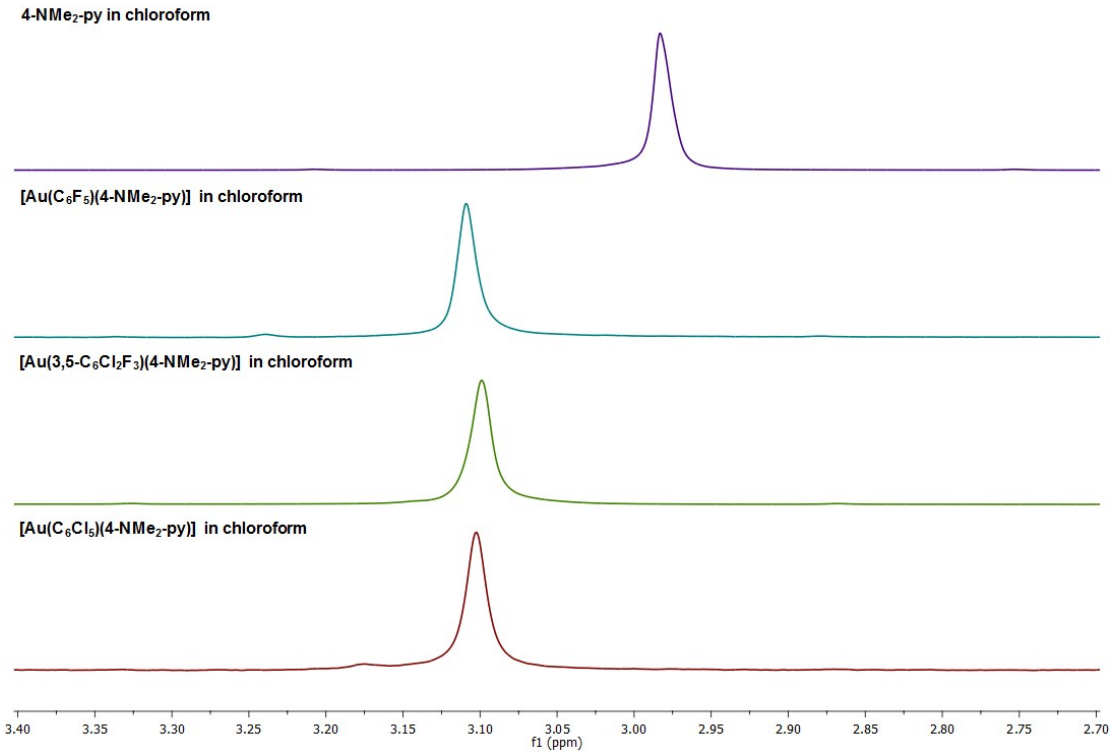


Figure S2. ^{1}H NMR spectra of complexes **1-3** and free DMAP in $CDCl_3$ for the –NMe_2 signals.

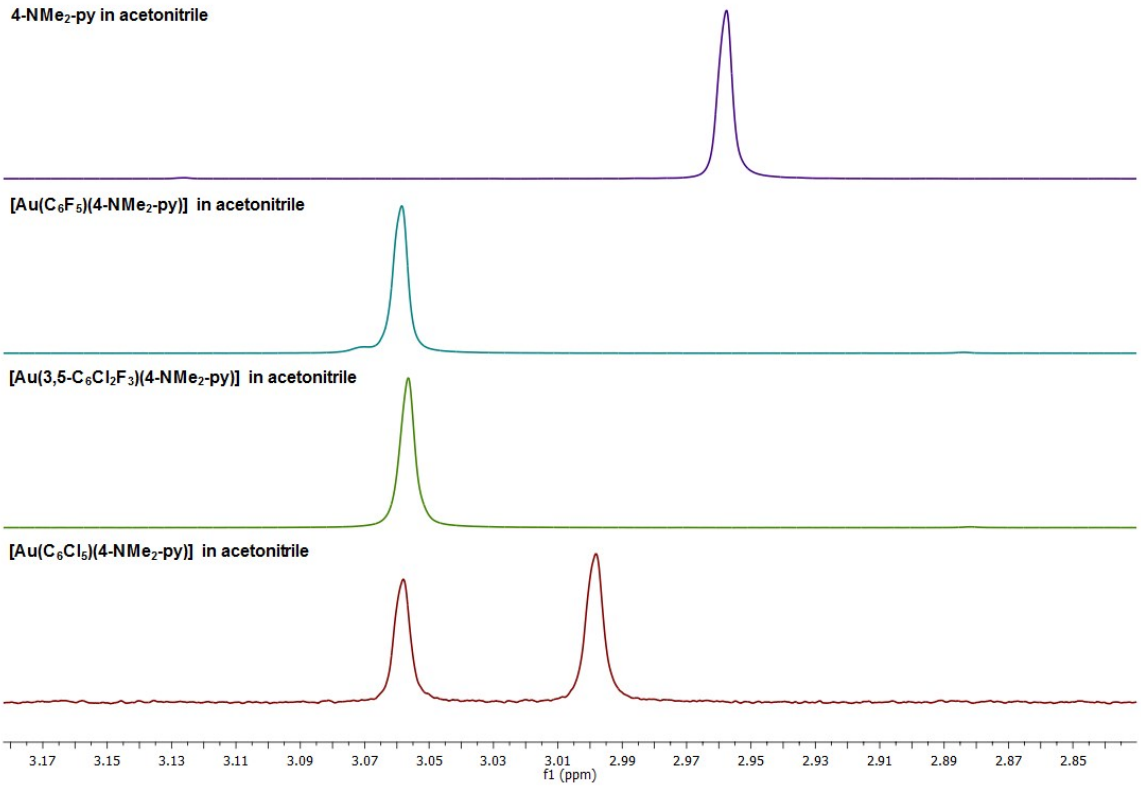


Figure S3. ^{1}H NMR spectra of complexes **1**-**3** and free DMAP in CD_3CN for the $-NMe_2$ signals.

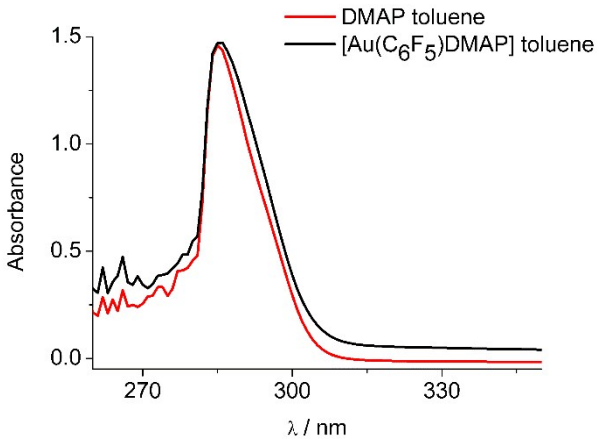


Figure S4. UV-Vis spectra of complex **1** and free DMAP in $1.2x10^{-4}$ M and $7.5x10^{-4}$ M toluene solutions, respectively.

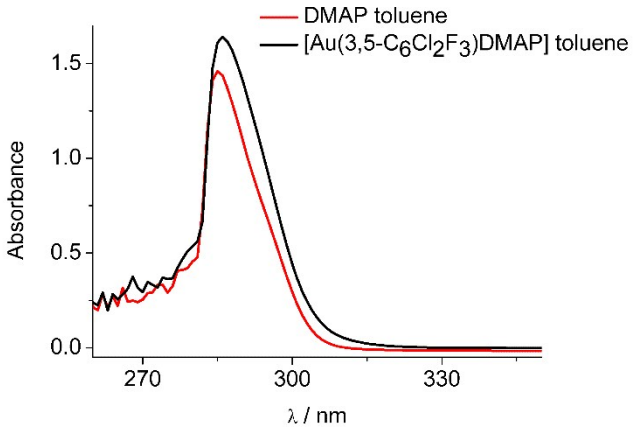


Figure S5. UV-Vis spectra of complex **2** and free DMAP in 6.5×10^{-5} M and 7.5×10^{-4} M toluene solutions, respectively.

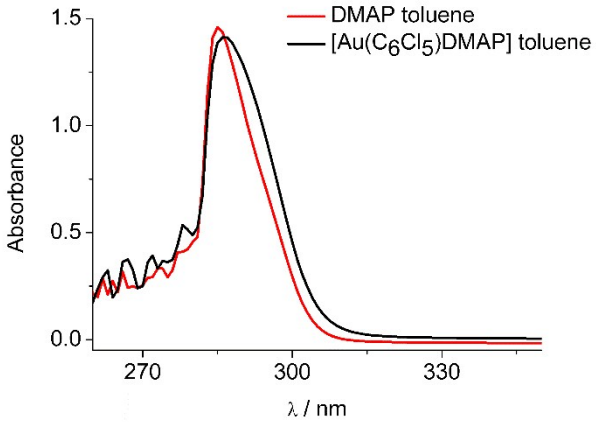


Figure S6. UV-Vis spectra of complex **3** and free DMAP in 4.7×10^{-5} M and 7.5×10^{-4} M toluene solutions, respectively.

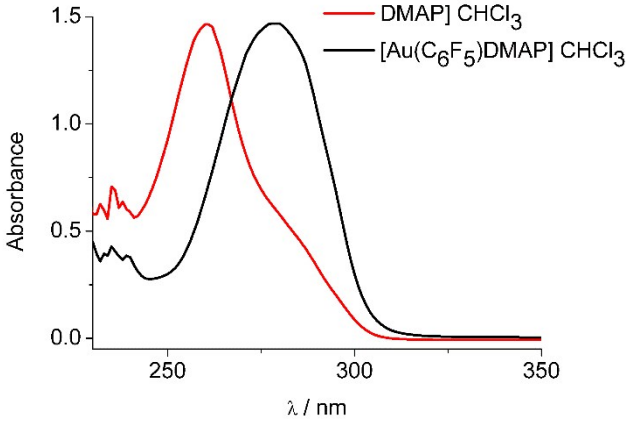


Figure S7. UV-Vis spectra of complex **1** and free DMAP in 4.8×10^{-5} M and 9.4×10^{-5} M chloroform solutions, respectively.

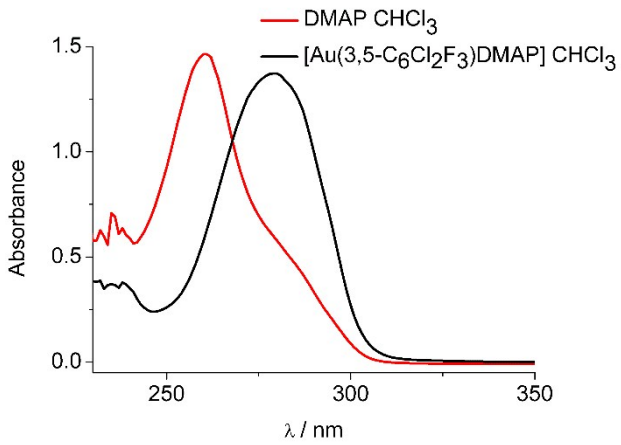


Figure S8. UV-Vis spectra of complex **2** and free DMAP in 4.4x10^{-5} M and 9.4x10^{-5} M chloroform solutions, respectively.

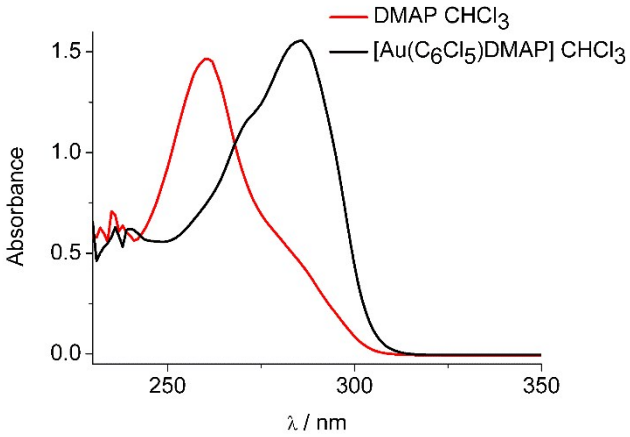


Figure S9. UV-Vis spectra of complex **3** and free DMAP in 4.4x10^{-5} M and 7.5x10^{-4} M chloroform solutions, respectively.

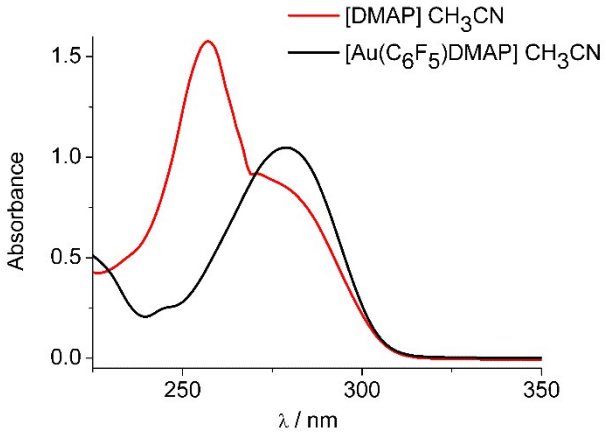


Figure S10. UV-Vis spectra of complex **1** and free DMAP in 4.1x10^{-5} M and 1.2x10^{-4} M acetonitrile solutions, respectively.

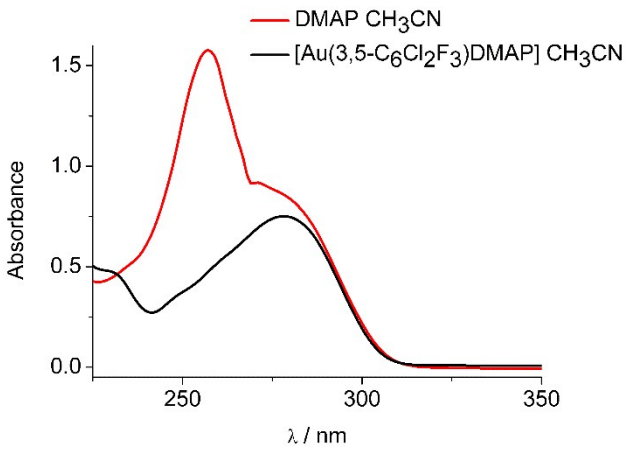


Figure S11. UV-Vis spectra of complex **2** and free DMAP in 3.2×10^{-5} M and 1.2×10^{-4} M acetonitrile solutions, respectively.

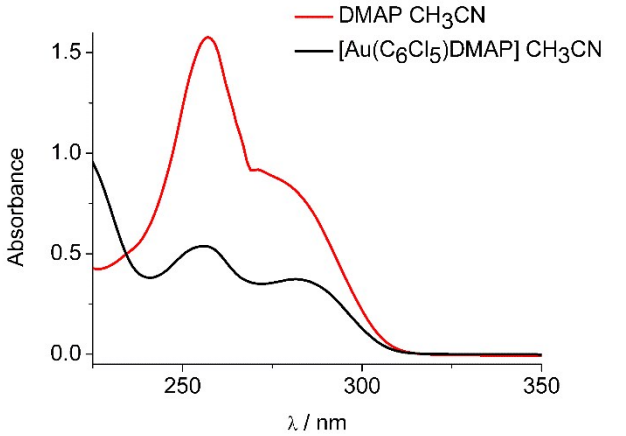


Figure S12. UV-Vis spectra of complex **3** and free DMAP in 2.7×10^{-5} M and 1.2×10^{-4} M acetonitrile solutions, respectively.

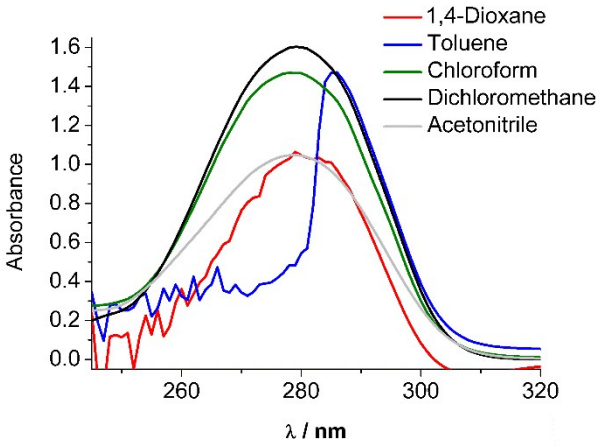


Figure S13. UV-Vis spectra of complex [Au(C_6F_5(DMAP)] (**1**) in solvents of different polarities.

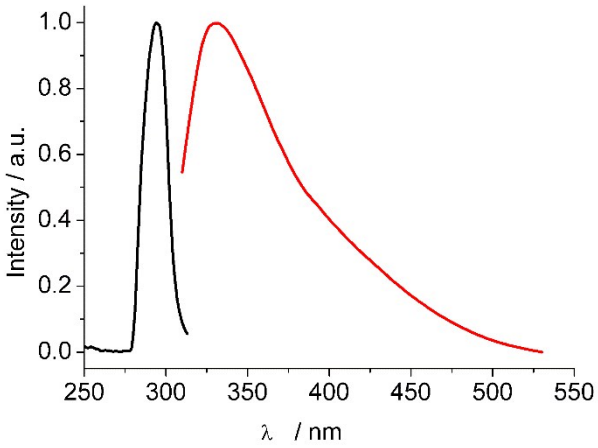


Figure S14. Excitation and emission spectra of DMAP in toluene solution.

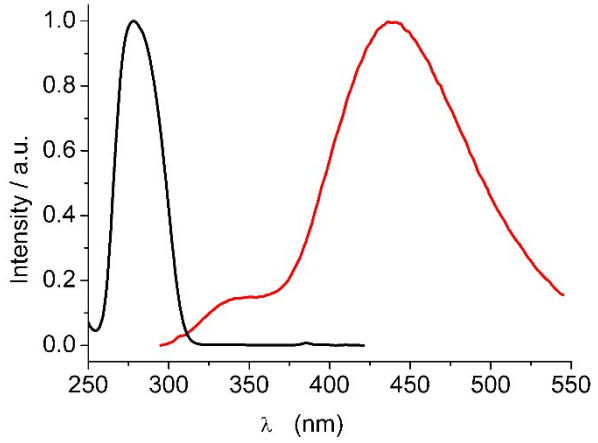


Figure S15. Excitation and emission spectra of DMAP in acetonitrile solution.

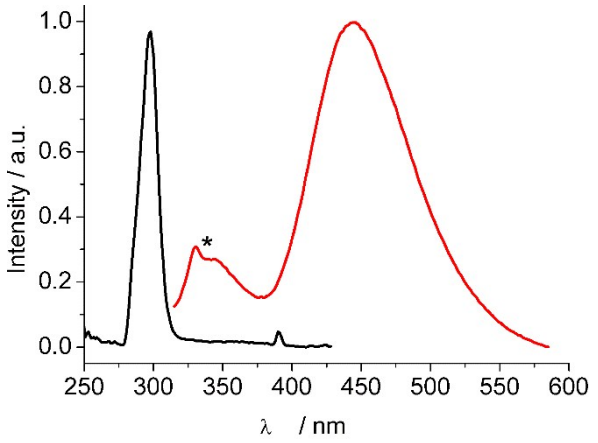


Figure S16. Excitation and emission spectra of complex **1** in toluene solution.

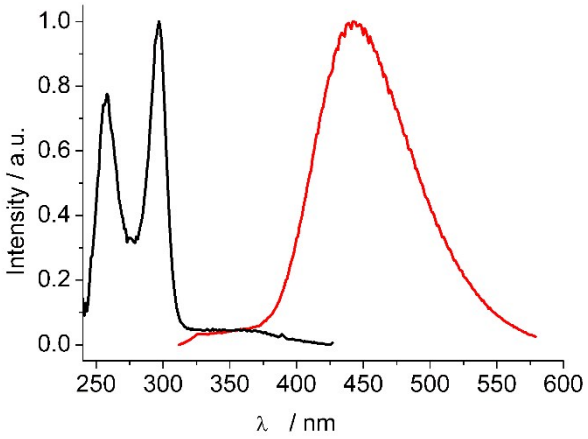


Figure S17. Excitation and emission spectra of complex **1** in chloroform solution.

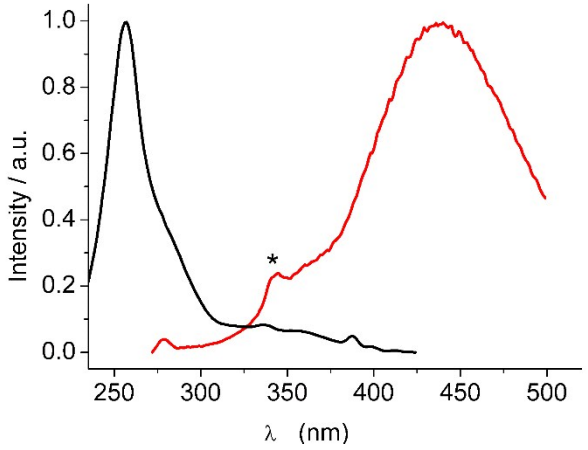


Figure S18. Excitation and emission spectra of complex **1** in acetonitrile solution (*solvent signal).

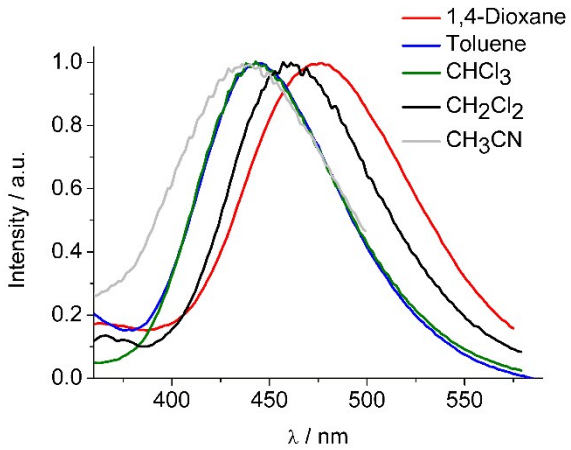


Figure S19. Emission spectra of complex [Au(C_6F_5(DMAP)] (**1**) in solvents of different polarities.

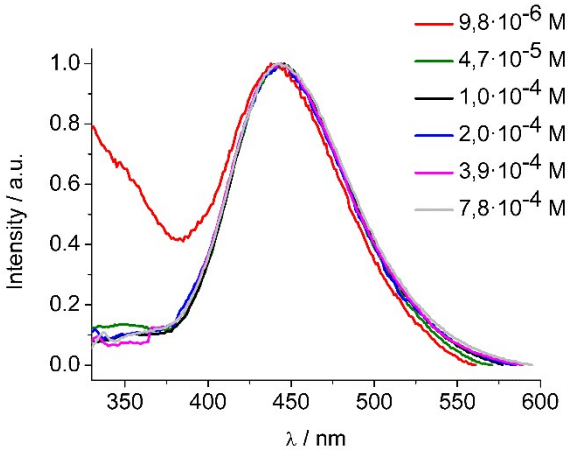


Figure S20. Emission spectra of complex [Au(C_6F_5(DMAP)] (**1**) in different concentration in toluene.

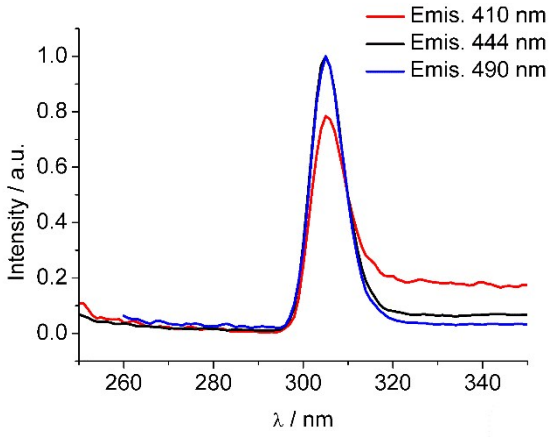


Figure S21. Excitation spectra of complex [Au(C_6F_5(DMAP)] (**1**) at different emission wavelenghts in toluene.

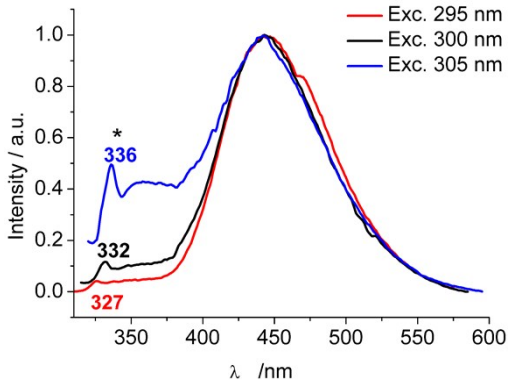


Figure S22. Emission spectra of complex [Au(C_6F_5(DMAP)] (**1**) at different excitation wavelenghts in toluene (* instrumental artefact).

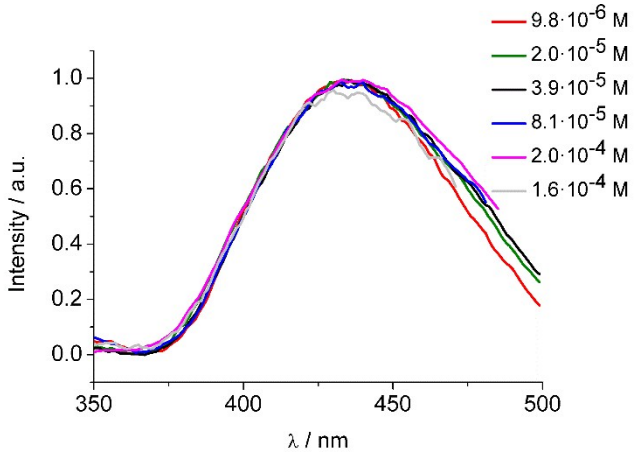


Figure S23. Emission spectra of complex [Au(C_6F_5(DMAP)] (**1**) in different concentration in acetonitrile.

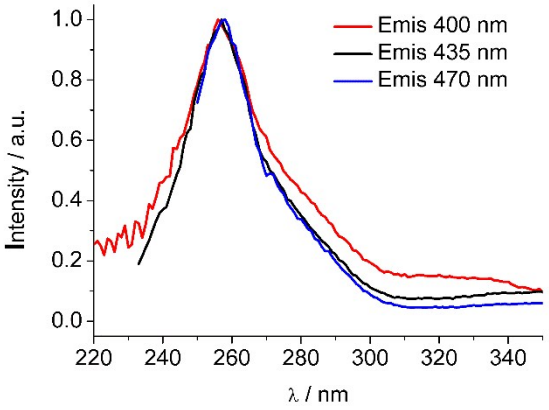


Figure S24. Excitation spectra of complex [Au(C_6F_5(DMAP)] (**1**) at different emission wavelenghts in acetonitrile.

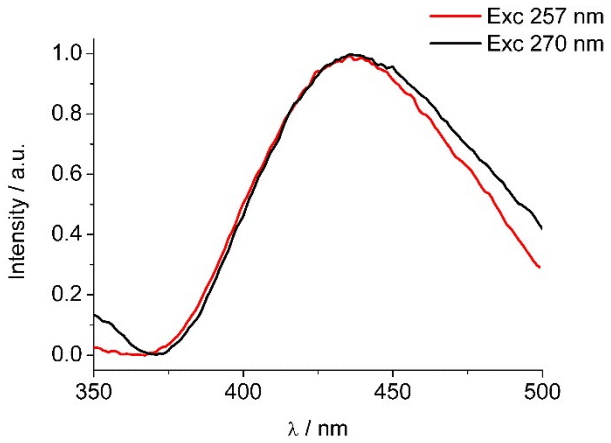


Figure S25. Emission spectra of complex [Au(C_6F_5(DMAP)] (**1**) at different excitation wavelenghts in acetonitrile.

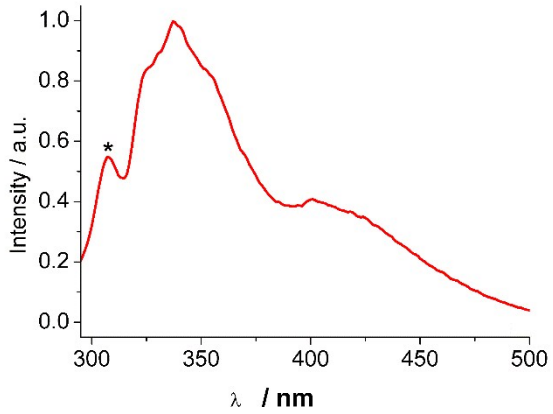


Figure S26. Emission spectrum of acetonitrile (* instrumental artefact).

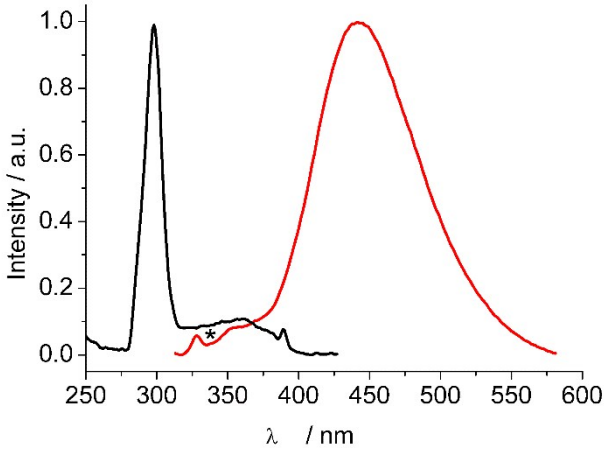


Figure S27. Excitation and emission spectra of complex **2** in toluene solution (* instrumental artefact).

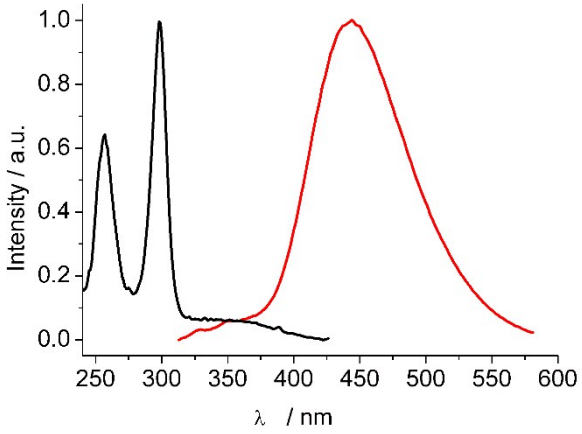


Figure S28. Excitation and emission spectra of complex **2** in chloroform solution.

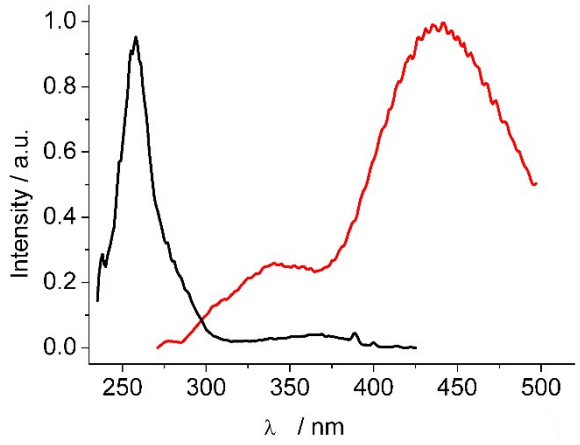


Figure S29. Excitation and emission spectra of complex **2** in acetonitrile solution.

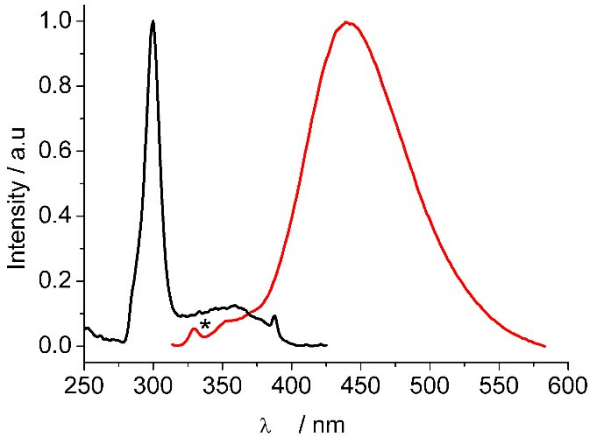


Figure S30. Excitation and emission spectra of complex **3** in toluene solution (* instrumental artefact).

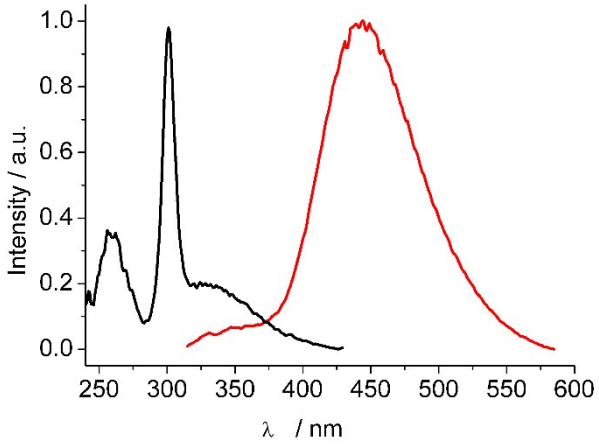


Figure S31. Excitation and emission spectra of complex **3** in chloroform solution.

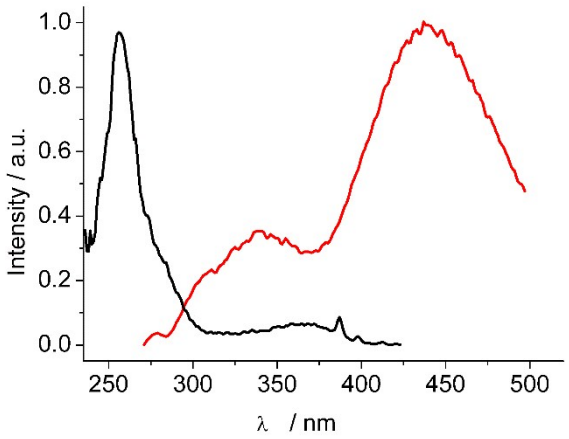


Figure S32. Excitation and emission spectra of complex **3** in acetonitrile solution.

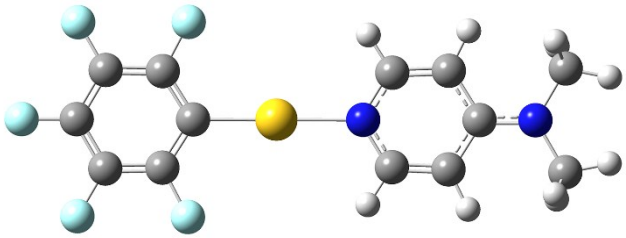
Table S1. Lifetime of complex [Au(C_6F_5(DMAP)] (**1**) in solvent of different polarity

	τ_1 (%) / ns	τ_2 (%) / ns
Toluene	1.3 (89)	6.7 (11)
Chloroform	1.3(90)	3.1(10)
Acetonitrile	3.5 (74)	6.8(26)

XYZ COORDINATES AND FIGURES OF THE FULLY OPTIMIZED COMPUTED STRUCTURES FOR THE CRITICAL POINTS FOR [Au(C_6F_5)DMAP] IN THE GAS PHASE, TOLUENE AND ACETONITRILE

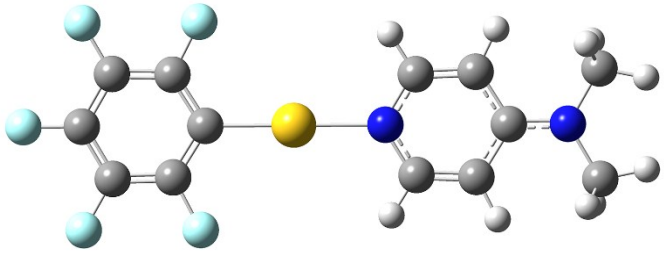
DFT (S_0) and TDDFT (S_1) CAM-B3LYP/TZVP optimisations in gas phase, toluene and acetonitrile

[Au(C_6F_5)DMAP]_S_0_gas



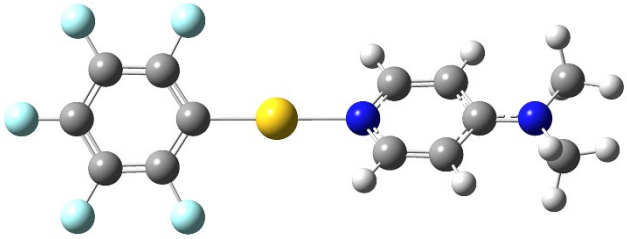
Au	-1.52421650	0.75498578	0.00000000
C	-1.45511750	0.75915178	-2.01863000
C	-1.73073450	-0.36859722	-2.76861700
C	-1.68964250	-0.38892122	-4.15044800
C	-1.35881650	0.76504778	-4.83381800
C	-1.07561750	1.91609978	-4.12461900
C	-1.12903550	1.88998078	-2.74330700
F	-2.05928550	-1.52318122	-2.15820700
F	-1.96434150	-1.50468722	-4.83248200
F	-1.31323150	0.76784078	-6.16661100
F	-0.75510450	3.03466778	-4.78161100
F	-0.84310950	3.04194778	-2.10704200
N	-1.59595050	0.75075478	2.09810500
C	-1.33280550	1.85624378	2.80940900
H	-1.08427150	2.74005178	2.23865100
C	-1.36674050	1.90187278	4.17858000
H	-1.14054550	2.83607778	4.66697600
C	-1.69155050	0.74504278	4.91355200
C	-1.96557450	-0.40876022	4.15355400
H	-2.22414950	-1.34492822	4.62170600
C	-1.90658550	-0.35757222	2.78542900
H	-2.11566950	-1.23904222	2.19556000
N	-1.73748750	0.74228078	6.26596900
C	-2.07637050	-0.47364122	6.98144300
H	-2.06010350	-0.27334322	8.04827600
H	-1.35990750	-1.27319522	6.77726200
H	-3.07635550	-0.82851622	6.71996200
C	-1.44747150	1.95502778	7.00780900
H	-1.53662650	1.75048178	8.07022800
H	-2.14790050	2.75596778	6.75847700
H	-0.43176850	2.31012878	6.81662200

[Au(C_6F_5)DMAP]_S_0_toluene



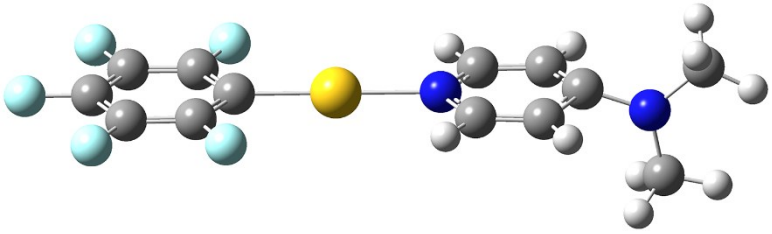
Au	-0.35612535	0.24216525	0.00000000
C	-0.28678235	0.24888925	-2.02177400
C	0.89912465	0.36889125	-2.72133300
C	0.97262565	0.37616825	-4.10155900
C	-0.18744235	0.25855525	-4.84076000
C	-1.39657635	0.13610725	-4.18571400
C	-1.42059635	0.13384625	-2.80367500
F	2.06776665	0.48738625	-2.05864800
F	2.14754465	0.49506625	-4.73010200
F	-0.14056735	0.26310825	-6.17479400
F	-2.52412235	0.02173925	-4.89642500
F	-2.63297635	0.01078625	-2.22568800
N	-0.42637335	0.23536725	2.09187200
C	0.68437765	0.38534725	2.83120500
H	1.60835865	0.50685725	2.28379200
C	0.68770465	0.38972225	4.20015700
H	1.62868565	0.51648325	4.71084900
C	-0.52106135	0.23088725	4.90939300
C	-1.67920335	0.07292425	4.12008800
H	-2.65213735	-0.05657775	4.56598100
C	-1.58404635	0.08210225	2.75445800
H	-2.46909935	-0.03799475	2.14578900
N	-0.56642635	0.23022525	6.25759200
C	-1.83380435	0.06031425	6.94652800
H	-1.66074735	0.09207125	8.01739700
H	-2.29477235	-0.90043175	6.70590900
H	-2.53699435	0.85701325	6.69345000
C	0.65248965	0.39687625	7.02967600
H	0.40778765	0.37002725	8.08658400
H	1.13273065	1.35476325	6.81719300
H	1.36759465	-0.40365875	6.82694000

[Au(C_6F_5)DMAP]_S_0_acetonitrile



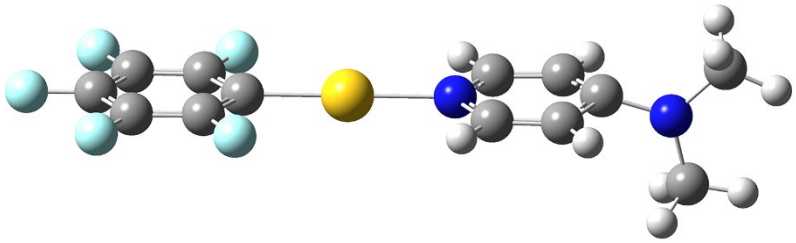
Au	-1.11111109	2.19373228	0.00000000
C	-1.03736309	2.19776628	-2.02465800
C	-0.79327109	1.05505728	-2.76270200
C	-0.73466709	1.03367628	-4.14309800
C	-0.92698809	2.20538928	-4.84606600
C	-1.17405109	3.37329328	-4.15393900
C	-1.22434709	3.34433628	-2.77336100
F	-0.59610209	-0.12653572	-2.13909300
F	-0.49421809	-0.10376672	-4.80728600
F	-0.87442509	2.20909828	-6.18068500
F	-1.36158309	4.51443228	-4.82875400
F	-1.47031709	4.52255628	-2.16079500
N	-1.18450409	2.19175628	2.08713600
C	-0.63046509	3.18145328	2.80967200
H	-0.15365909	3.97309328	2.24931300
C	-0.64740209	3.22142028	4.17665900
H	-0.17738909	4.05594528	4.67144700
C	-1.27056909	2.18548628	4.90715900
C	-1.84908509	1.15359128	4.13536400
H	-2.34897509	0.31724728	4.59675000
C	-1.78222709	1.19940728	2.77004000
H	-2.22364409	0.41022528	2.17812900
N	-1.31029509	2.18185028	6.25141000
C	-1.96602409	1.09607728	6.96218600
H	-1.89041309	1.27727528	8.02908700
H	-1.49410009	0.13552028	6.74550300
H	-3.02452609	1.03140628	6.70189400
C	-0.69805909	3.26380228	7.00551000
H	-0.83393209	3.07531428	8.06515800
H	-1.15845309	4.22522028	6.76867700
H	0.37345191	3.33155728	6.80639800

[Au(C_6F_5)DMAP]_S_1-ICT_gas



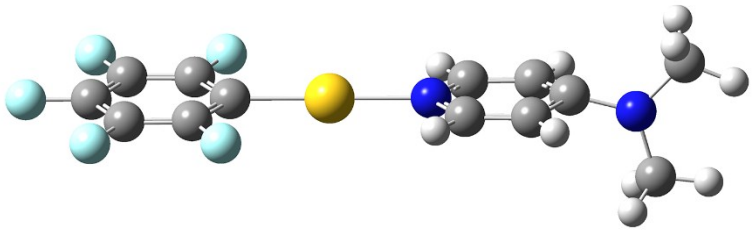
Au	0.24216524	-0.12820513	0.00000000
C	0.24777524	-0.01599813	-2.02009400
C	-0.75665076	-0.56471413	-2.79530500
C	-0.77444876	-0.50014113	-4.17640000
C	0.25505424	0.14126387	-4.83661800
C	1.28085924	0.70505787	-4.10379700
C	1.25594824	0.61544087	-2.72420800
F	-1.79008176	-1.20374213	-2.21197200
F	-1.77087876	-1.04768713	-4.88131700
F	0.25840924	0.21583687	-6.16980200
F	2.28043724	1.32792987	-4.73819600
F	2.28564124	1.18617687	-2.06799900
N	0.23398524	-0.23977113	2.07924500
C	1.22161324	0.32712387	2.82862300
H	2.01142224	0.81227587	2.27246000
C	1.25932324	0.29892387	4.18400800
H	2.08373624	0.76640487	4.70446300
C	0.24348224	-0.42585813	4.89421900
C	-0.84568076	-0.93537513	4.10950700
H	-1.68206876	-1.44172013	4.57117800
C	-0.78059476	-0.84686713	2.75776300
H	-1.55887476	-1.28118013	2.14609100
N	-0.00372376	-0.08552613	6.24138100
C	0.46697324	-0.95173713	7.28370200
H	0.21044824	-0.57308613	8.26920000
H	1.54918124	-1.06176213	7.17802300
H	0.04054624	-1.94542913	7.12492400
C	-0.72423576	1.12388587	6.55394300
H	-0.84112376	1.26159087	7.62460700
H	-1.69719276	1.07810187	6.05894300
H	-0.18671476	1.96489387	6.10959100

[Au(C_6F_5)DMAP]_S_1-ICT_toluene



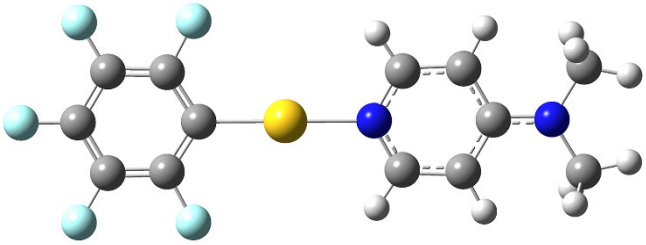
Au	-0.45580139	1.42450148	0.00596677
C	-0.32779739	1.50905948	-2.01425523
C	0.61726861	0.79918448	-2.73105423
C	0.72340661	0.84107048	-4.10865623
C	-0.15153439	1.62759248	-4.83068223
C	-1.11338839	2.35579748	-4.15986423
C	-1.17980339	2.28160048	-2.78117923
F	1.50424561	0.01024048	-2.08847823
F	1.65942861	0.13235948	-4.75250923
F	-0.06844039	1.68353048	-6.16318723
F	-1.96527239	3.12121848	-4.85367023
F	-2.14351439	3.01914048	-2.19005023
N	-0.58831139	1.34071748	2.07439877
C	0.29999361	0.61960648	2.82251077
H	1.06354161	0.09367848	2.26680977
C	0.25905861	0.53147148	4.17394677
H	0.99689761	-0.06131052	4.69630477
C	-0.80820539	1.17946848	4.88285777
C	-1.68362539	2.01181148	4.10685977
H	-2.47273239	2.58236848	4.57631377
C	-1.55053739	2.02977448	2.75869577
H	-2.23480839	2.60719648	2.15309777
N	-0.65302639	1.44514748	6.25147477
C	-1.32205339	0.61158148	7.21314677
H	-1.11970539	0.93364348	8.22999177
H	-0.99577539	-0.41949852	7.05896477
H	-2.39336039	0.63643748	7.00222477
C	0.17061661	2.55235948	6.67803377
H	0.21312261	2.62704048	7.75968777
H	-0.23733239	3.46702748	6.24192677
H	1.16896461	2.41664748	6.25734077

[Au(C_6F_5)DMAP]_S_1-ICT_acetonitrile



Au	-0.64102563	1.59544165	0.00000000
C	-0.61614163	1.66926565	-2.02691800
C	-1.58515663	1.06780165	-2.80804700
C	-1.59123663	1.10631165	-4.18923300
C	-0.58319863	1.77656165	-4.85151900
C	0.40862137	2.39374265	-4.11708600
C	0.37058437	2.32683465	-2.73750600
F	-2.60276963	0.39375165	-2.22713300
F	-2.55832963	0.50420765	-4.89395500
F	-0.56784463	1.82746365	-6.18690600
F	1.39110337	3.04715765	-4.75132400
F	1.37398537	2.95354965	-2.08351600
N	-0.66642063	1.52032465	2.06605900
C	0.34181237	2.06516065	2.81892000
H	1.14709637	2.52592565	2.26392500
C	0.37467137	2.04426165	4.17204100
H	1.20171937	2.49679265	4.70063700
C	-0.67673463	1.37467965	4.88624900
C	-1.77435363	0.87767965	4.10390000
H	-2.62895363	0.41722165	4.57907500
C	-1.70769663	0.95221665	2.75396400
H	-2.50414263	0.54269765	2.14835100
N	-0.85861263	1.63135165	6.24433300
C	-0.37647663	0.68512065	7.21761600
H	-0.58929963	1.01596265	8.22855700
H	0.69758837	0.55941465	7.06778500
H	-0.84627463	-0.27979735	7.01759600
C	-1.52980163	2.84288465	6.66118000
H	-1.58819363	2.91141765	7.74171000
H	-2.52795363	2.84731765	6.21878900
H	-0.98429363	3.69297565	6.24729700

[Au(C_6F_5)DMAP]_S_1-LE_toluene



Au	-1.48453536	2.73008174	-0.01630344
C	-1.41695136	2.73475374	-2.03912044
C	-0.22910536	2.83160174	-2.74007444
C	-0.15758136	2.83633374	-4.12019144
C	-1.32127136	2.74046774	-4.85723344
C	-2.53224236	2.64176574	-4.20109344
C	-2.55463736	2.64087174	-2.81927644
F	0.94150364	2.92793874	-2.07929644
F	1.01791764	2.93208174	-4.75127244
F	-1.27613136	2.74322874	-6.19081744
F	-3.66198436	2.54895374	-4.91111444
F	-3.76739236	2.54165274	-2.23962144
N	-1.55438136	2.72403774	2.05628056
C	-0.41834636	2.88432174	2.75769456
H	0.49120264	3.00917774	2.19448956
C	-0.42030336	2.89050474	4.18325756
H	0.50825264	3.02461574	4.70929856
C	-1.65034436	2.71745174	4.83793356
C	-2.83266336	2.54771874	4.09872756
H	-3.79520536	2.41037074	4.55854756
C	-2.73556536	2.56006874	2.67692456
H	-3.60382936	2.43751174	2.05143356
N	-1.69777136	2.71369774	6.20638356
C	-2.95402736	2.52583474	6.90970556
H	-2.77685736	2.57049574	7.97781056
H	-3.38661736	1.55678074	6.65872156
H	-3.66305536	3.30607974	6.63219056
C	-0.49195336	2.89213274	6.99496656
H	-0.74342836	2.85391374	8.04823456
H	-0.03314636	3.85568574	6.77110656
H	0.22697264	2.10382674	6.76993356

Table S2. Calculated (TDDFT) main angles and main distances of [Au(C_6F_5)(DMAP)] (**1**) in LE (S_1) excited state in toluene.

τ	θ	ω	C9-C8-N1-C5 C13-C8-N1-C1	C1-C2 C4-C5	C2-C3 C3-C4	C5-N1 N1-C1	C3-N2
0.54	0.10	0.31	3.28 3.24	1.425 1.425	1.405 1.404	1.345 1.345	1.369

Table S3. Population Analysis for model of complex [Au(C_6F_5(DMAP)] (**1**).

Solvent	Orbital[a]	Au	C_6F_5	Py	NMe_2
Toluene	LUMO	7	7	76	11
	HOMO	14	30	29	27
Acetonitrile	LUMO	19	19	53	8
	HOMO	6	5	44	45

[a]Contribution from each part of the molecule to the frontier orbitals (%).

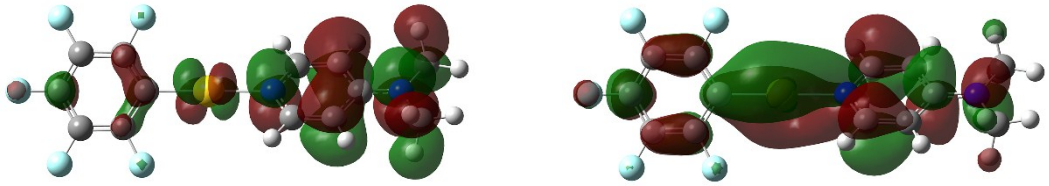
Table S4. TD-DFT Singlet−Singlet Excitation Calculation for model of complex [Au(C_6F_5(DMAP)] (**1**)

Solvent	Exc.	λ_{cal} (nm)	f	Contributions[b]
Toluene	$S_0 \rightarrow S_2$	243.33	1.0407	HOMO→LUMO (81.1)
Acetonitrile	$S_0 \rightarrow S_2$	242.77	0.9657	HOMO→LUMO (78.4)

[b]Oscillator strength (f) shows the mixed representation of both velocity and length representations. [c]Value is $2 \times |coeff|^2 \times 100$.

HOMO LUMO

Figure S33. Frontier molecular orbitals for model of complex [Au(C_6F_5(DMAP)] (**1**) in toluene.



HOMO LUMO

Figure S34. Frontier molecular orbitals for model of complex [Au(C_6F_5(DMAP)] (**1**) in acetonitrile.

Table S5. DFT calculation of dipole moment in Ground, ICT and LE state of complex [Au(C_6F_5(DMAP)] (**1**) in toluene and acetonitrile.

	μ_{GS}	μ_{ICT}	μ_{LE}
Toluene	17.3	24.0	19.9
Acetonitrile	18.5	25.8	-