Syntheses and Photophysical Properties of Luminescent Monocyclometalated Gold(III) *cis*-Dialkynyl Complexes

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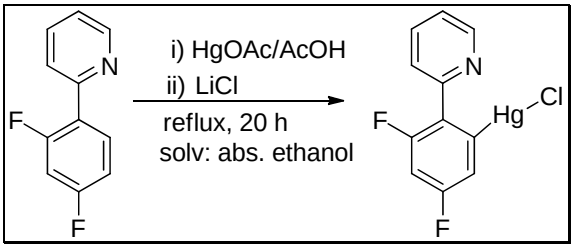
Synthetic details and spectroscopic data.

(3,5-difluoro-2-(pyridin-2-yl)phenyl)mercury(II) chloride (step-1for **D**)



2-(2,4-difluorophenyl)pyridine (1.0 g, 5.23 mmol) in absolute ethanol (6.0 mL) was added to a stirred solution of mercuric acetate (1.8 g, 5.64 mmol) in ethanol (30.0 mL) containing acetic acid (0.4 mL). After being stirred at RT overnight, the reaction mixture was refluxed for 20 h, filtered hot and evaporated to dryness under reduced pressure. The residue thus obtained was re-dissolved in warm ethanol (15 mL) and filtered into a solution of lithium choride (0.554 g, 13.0 mmol) in ethanol (35 mL). The mixture was allowed to stand at RT overnight and filtered, the collected solids were finally washed with cold water (30.0 mL). Recrystallization from ethanol twice gave the title product as colorless needles, Yield = 0.25 g, 11%; IR (KBr): ν (Hg–Cl) 342 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 6.81 - 6.87 (m, 1H), 7.07 (d, J = 4.0 Hz 1H), 7.34 - 7.37 (m, 1H), 7.78 (t, J = 7.8 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) = 105.1, 120.5, 123.7, 125.1, 125.4, 138.2, 148.4, 151.7, 154.8, 162.5 (d, $^{1}J_{C\text{-}F}$ = 258.7 Hz), 163.0 (d, $^{1}J_{C\text{-}F}$ = 256.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): δ (ppm) = -108.3 (dd, $^{4}J_{Hg\text{-}F}$ = 248.0 Hz, $^{4}J_{F\text{-}F}$ = 8.0 Hz, 1F), -110.1 (dd, $^{4}J_{Hg\text{-}F}$ = 161.0 Hz, $^{4}J_{F\text{-}F}$ = 8.0 Hz, 1F); ^{199}Hg (89 MHz, rel. to Me_2Hg, $CDCl_3$, 298 K): δ (ppm) = -1000.0 (dd, $^{4}J_{Hg\text{-}F}$ = 248.0, 161.0 Hz).

Caution: Although we had no prior experience, mercuric chloride derivatives are potentially toxic and should be handled with care.

Thermogravimetric Analysis (TGA)

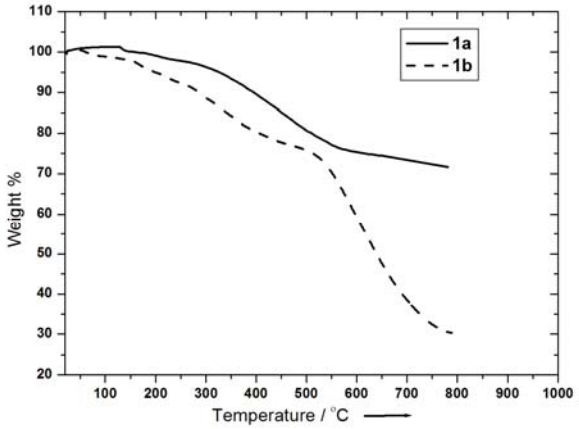


Figure S1. Thermal gravimetric traces of the complexes measured under N_2 atmosphere, rate of heating 5°C/min for **1a** and 1°C/min for **1b** from 25 °C to 800 °C.

X-ray diffraction studies of 1b, 1c and 4a.

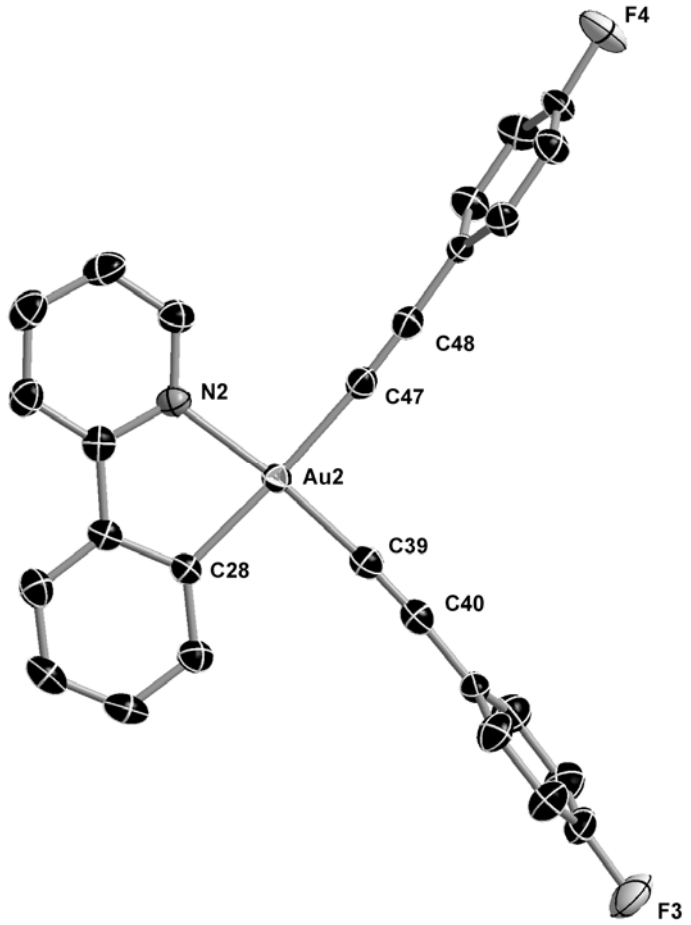


Figure S2. Thermal ellipsiod plot of **1b** (50% probability level of thermal ellipsoids) with selective atomic numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): N(2)-Au(2) 2.068(2), C(28)-Au(2) 2.043(2), C(47)-Au(2) 2.031(2), C(39)-Au(2) 1.973(3), C(28)-Au(2)-N(2) 81.00(9), C(39)-Au(2)-C(47) 90.94(9), C(47)-Au(2)-N(2) 94.98(9), C(39)-Au(2)-C(28) 93.09(10).

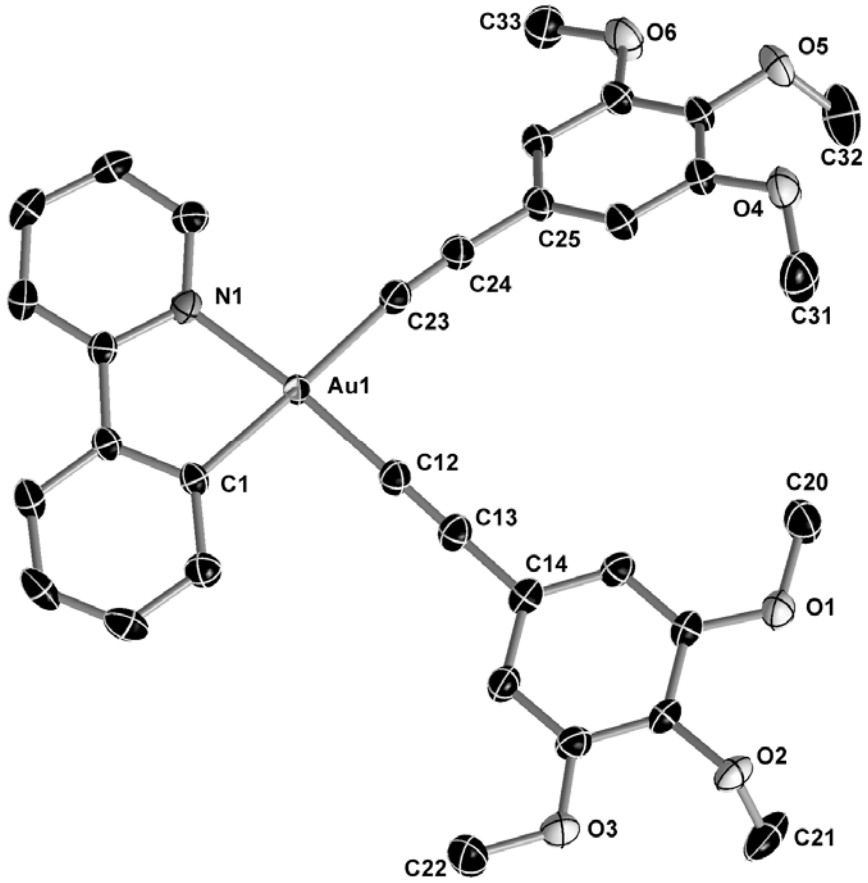


Figure S3. Thermal ellipsiod plot of **1c** (50% probability level of thermal ellipsoids) with selective atomic numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)-Au(1) 2.0566(12), C(1)-Au(1) 2.0380(13), C(12)-Au(1) 1.9724(16), C(23)-Au(1) 2.0390(16), C(1)-Au(1)-N(1) 80.89(5), C(12)-Au(1)-C(1) 93.81(6), C(12)-Au(1)-C(23) 88.47(6), C(23)-Au(1)-N(1) 96.76(6).

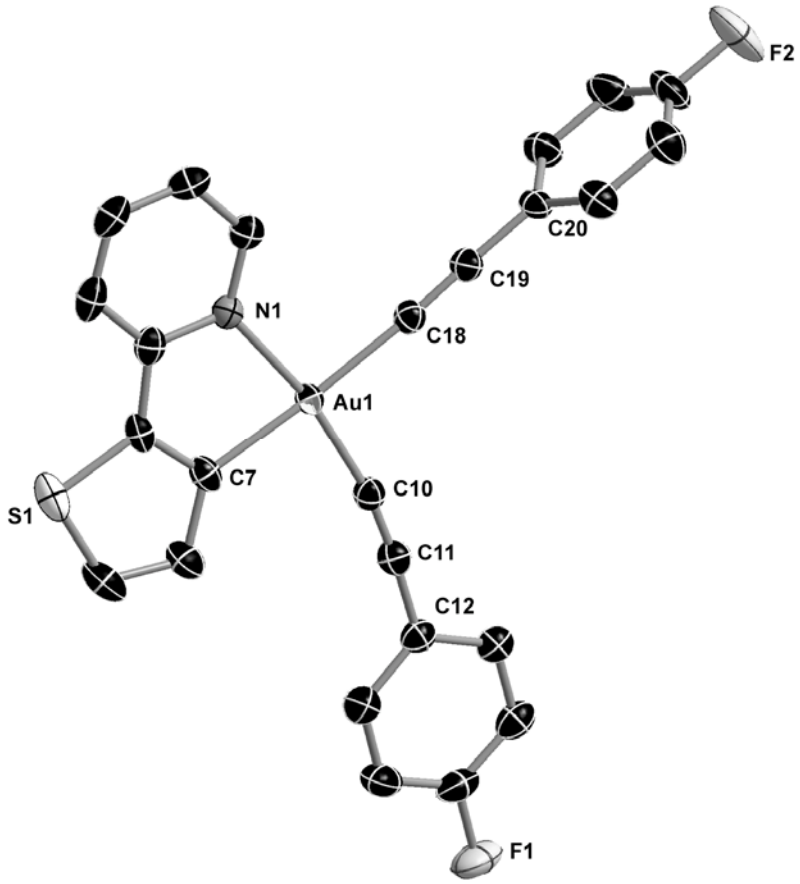


Figure S4. Thermal ellipsiod plot of **4a** (30% probability level of thermal ellipsoids) with selective atomic numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)-Au(1) 2.084(3), C(7)-Au(1) 2.027(3), C(18)-Au(1) 2.033(3), C(10)-Au(1) 1.966(4), C(7)-Au(1)-N(1) 80.99(13), C(10)-Au(1)-C(18) 95.28(14), C(18)-Au(1)-N(1) 94.71(12), C(10)-Au(1)-C(7) 89.03(14).

Table S1. Crystallographic data for compounds **1a**, **1e**, **3a** and **5a**.

	1a	**1e**	**3a**	**5a**
empirical formula	$C_{27}H_{18}AuN$	$C_{33}H50AuNSi_2$	$C_{29}H_{18}AuN$	$2(C_{26}H_{16}AuF_2NS)$, CH_2Cl_2
formula weight ($g \cdot mol^{-1}$)	553.39	713.89	577.41	1303.80
temperature (K)	183(2)	183(2)	183(2)	183(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system, space group	monoclinic, *P* $2_1/c$	triclinic, *P* -1	orthorhombic, *P* b c a	monoclinic, *P* $2_1/c$
a (Å)	10.4792(2)	7.3589(2)	17.1690(2)	12.1145(1)
b (Å)	18.0604(2)	13.9624(4)	13.3040(1)	17.9931(1)
c (Å)	11.6604(2)	18.0915(4)	18.4488(1)	22.1153(2)
α (deg)	90	69.459(2)	90	90
β (deg)	109.518(2)	85.021(2)	90	99.232(1)
γ (deg)	90	76.161(2)	90	90
volume ($Å^3$)	2080.02(6)	1690.14(8)	4214.01(6)	4758.19(7)
Z, density (calcd) ($Mg \cdot m^{-3}$)	4, 1.767	2, 1.403	8, 1.820	4, 1.820
abs coefficient (mm^{-1})	7.085	4.443	6.998	6.414
F(000)	1064	724	2224	2504
crystal size (mm^3)	0.37 x 0.32 x 0.09	0.45 x 0.10 x 0.07	0.34 x 0.14 x 0.11	0.26 x 0.24 x 0.04
θ range (deg)	2.53 to 30.50	2.85 to 30.51	2.51 to 32.58	2.45 to 28.28
reflections collected	29969	31474	58657	69869
reflections unique	6351 / [R_{int} = 0.0310]	10324 / [R_{int} = 0.0357]	7663 / [R_{int} = 0.0374]	11791 / [R_{int} = 0.0428]
completeness to θ (%)	99.9	99.9	100.0	99.9
absorption correction	analytical	analytical	analytical	analytical
max/min transmission	0.551 and 0.130	0.777 and 0.224	0.499 and 0.182	0.793 and 0.293
data / restraints / parameters	5209 / 0 / 262	8324 / 0 / 492	5188 / 0 / 280	9001 / 0 / 588
goodness-of-fit on F^2	1.005	0.909	0.921	0.908
final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0210, 0.0446	0.0269, 0.0436	0.0236, 0.0477	0.0243, 0.0401
R_1 and wR_2 indices (all data)	0.0312, 0.0459	0.0387, 0.0447	0.0463, 0.0500	0.0405, 0.0416

The unweighted R-factor is $R_1 = \sum(Fo - Fc)/\sum Fo$; $I > 2\,\sigma(I)$ *and the weighted R-factor is* $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$

Table S2. Crystallographic data for compounds **1b**, **1c**, and **4a**.

	1b	**1c**	**4a**
empirical formula	$2(C_{27}H_{16}AuF_2N), CH_2Cl_2$	$C_{33}H_{30}AuNO_6$	$C_{25}H_{14}AuF_2NS$
formula weight ($g \cdot mol^{-1}$)	1263.68	733.55	595.41
temperature (K)	183(2)	183(2)	183(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system, space group	triclinic, *P* -1	triclinic, *P* -1	triclinic, *P* -1
a (Å)	12.0324(2)	8.1641(1)	10.2423(2)
b (Å)	14.0679(3)	12.4453(2)	13.9037(2)
c (Å)	14.9710(3)	14.3191(2)	15.1281(2)
α (deg)	77.398(2)	93.756(1)	98.309(1)
β (deg)	71.229(2)	90.607(1)	103.044(1)
γ (deg)	72.866(2)	101.769(1)	95.233(1)
volume ($Å^3$)	2271.46(8)	1420.82(3)	2059.51(6)
Z, density (calcd) ($Mg \cdot m^{-3}$)	2, 1.848	2, 1.715	4, 1.920
abs coefficient (mm^{-1})	6.626	5.224	7.274
F(000)	1212	724	1136
crystal size (mm^3)	0.26 x 0.09 x 0.04	0.50 x 0.20 x 0.10	0.35 x 0.28 x 0.11
θ range (deg)	2.64 to 30.51	2.55 to 32.57	2.64 to 28.28
reflections collected	42000	50003	45341
reflections unique	13858 / [R_{int} = 0.0340]	10343 / [R_{int} = 0.0257]	10236 / [R_{int} = 0.0249]
completeness to θ (%)	99.9	100.0	99.9
absorption correction	analytical	analytical	analytical
max/min transmission	0.803 and 0.332	0.603 and 0.199	0.485 and 0.158
data / restraints / parameters	10032 / 0 / 586	9337 / 0 / 376	8762 / 35 / 541
goodness-of-fit on F^2	0.847	1.017	1.042
final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0228, 0.0357	0.0157, 0.0361	0.0233, 0.0536
R_1 and wR_2 indices (all data)	0.0401, 0.0369	0.0192, 0.0364	0.0297, 0.0547

The unweighted R-factor is $R_1 = \sum(Fo - Fc)/\sum Fo$; I > 2 σ(I) and the weighted R-factor is $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/}$

X-ray diffraction details

Relevant details about the structure refinements are given in Tables S3 and S4, and selected geometrical parameters are included in the captions of the corresponding figures. Intensity data were collected at 183(2) K an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector, and a single wavelength Enhance X-ray source with MoK_α radiation, λ = 0.71073 Å).[1] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption corrections[2] were performed with the Oxford program suite *CrysAlisPro*.[3] The crystal structures were solved with SHELXS-97[4] using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL-97.[4] All programs used during the crystal structure determination process are included in the WINGX software.[5] The program PLATON[6] was used to check the result of the X-ray analyses. CCDC-798717-798723 contain the supplementary crystallographic data (excluding structure factors) for 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.

In the crystal structure of **1e**, the phenylpyridine ligand is positionally disordered but only the N1 and C7 atoms were refined as disordered atoms, occupying the same fixed positions with identical thermal parameters. The Si^iPr_3 groups are also disordered over two positions with *sof* of about 0.5. The asymmetric unit of **4a** contains two crystallographically independent $C_{25}H_{14}AuF_2NS$ molecules. It seems that one thienylpyridine is slightly disordered over two sets of positions in an approximate ratio of 90/10 % which results in the observed positive residual peak of 2.25 e.Å^{-3} corresponding to the second position of the S2 atom. Nevertheless, we considered that the disorder is not enough to be refineable and reliable. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, with C-H = 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methine H atoms, with C-H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene H atoms, and with C-H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

No classic hydrogen bonds were observed in any crystal structures.

Table S3. Summary of interplanar Au-Au distances of **1a-1c**, **1e**, **3a**, **4a** and **5a**.

Complex	Au-Au distance (Å)
[(N^C)Au(C≡CC_6H_5)$_2$] [N^C = 2-phenylpyridine] (**1a**)	6.7647(2) Å
[(N^C)Au(C≡CC_6H_4-4-F)$_2$] [N^C = 2-phenylpyridine] (**1b**)	4.7920(2) Å
[(N^C)Au(C≡C$C_9H_{11}O_3$)$_2$] [N^C = 2-phenylpyridine] (**1c**)	3.7285(1) Å
[(N^C)Au(C≡C-Si(*i*Pr)$_3$)$_2$] [N^C = 2-phenylpyridine] (**1e**)	5.2180(2) Å
[(N^C)Au(C≡CC_6H_5)$_2$] [N^C = benzo[*h*]quinoline] (**3a**)	7.6181(1) Å
[(N^C)Au(C≡CC_6H_4-4-F)$_2$] [N^C = 2-(2-thienyl)pyridine] (**4a**)	4.1468(2) Å
[(N^C)Au(C≡CC_6H_4-4-F)$_2$] [N^C = 2-(5-methyl-2-thienyl)pyridine] (**5a**)	4.3021(2) Å

Absorption and emission spectra of selected complexes (1b-1e and **2a).**

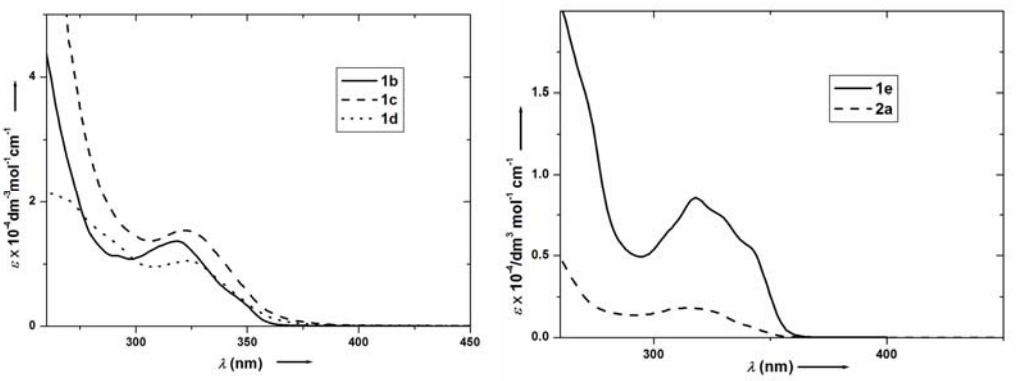


Figure S5. Electronic absorption spectra of **1b-1e** and **2a** in CH_2Cl_2 at RT.

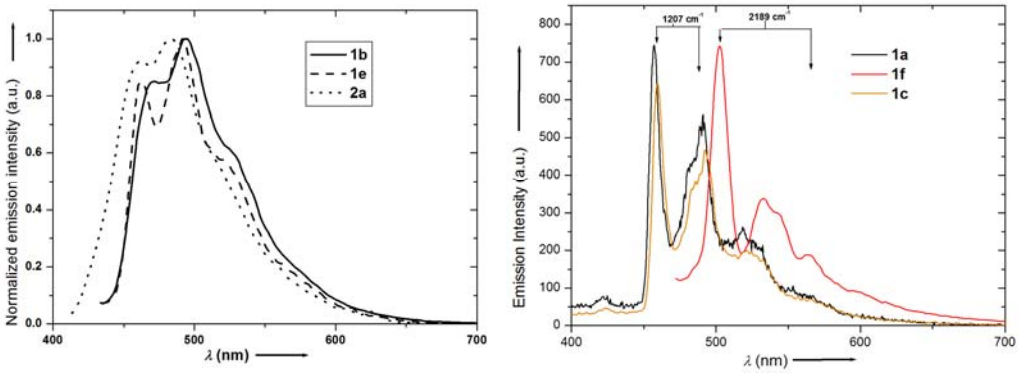


Figure S6. (*left*) Emission spectra of **1b**, **1e**, and **2a** in degassed CH_2Cl_2 at RT. (*right*) Emission spectra for selected compounds **1a**, **1c** and **1f** at 77 K in 2-MeTHF.

Cyclic voltammograms of selected complexes.

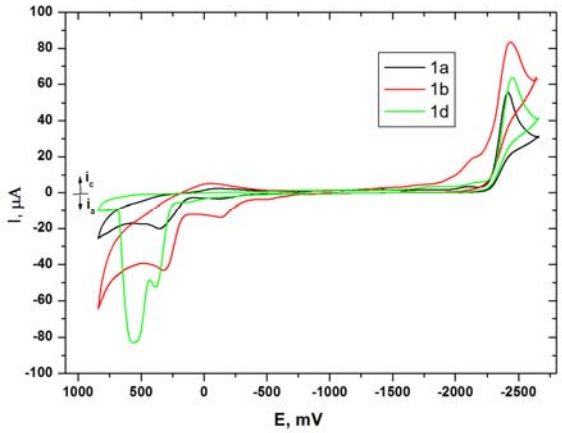


Figure S7. Cyclic voltammogram of **1a**, **1b** and **1d** in 0.1M [*n*Bu_4N][PF_6]; Au electrode; E *vs* $Fc^{0/+}$; scan rate = 100 mV/s; 20 ºC; CH_2Cl_2.

Electrochemical data of selected complexes.

Table S4. Summary of Cyclic Voltammetry for selected complexes in 0.1 M [*n*Bu_4N][PF_6]; Au electrode; E *vs* $Fc^{0/+}$; scan rate = 100 mV/s; 20 ºC, CH_2Cl_2.

Complex	Reduction $E_{p,c}$ (V)	Oxidation $E_{p,a}$ (V)
[(N^C)Au(C≡CC_6H_5)$_2$] [N^C = 2-phenylpyridine] (**1a**)	-2.41	0.36
[(N^C)Au(C≡CC_6H_4-4-F)$_2$] [N^C = 2-phenylpyridine] (**1b**)	-2.40	0.29
[(N^C)Au(C≡C$C_9H_{11}O_3$)$_2$] [N^C = 2-phenylpyridine] (**1c**)	-2.44	0.37, 0.56
[(N^C)Au(C≡CC_6H_4-C≡C-C_6H_5)$_2$] [N^C = 2-phenylpyridine] (**1f**)	-2.44	0.70
[(N^C)Au(C≡CC_6H_4-4-F)$_2$] [N^C = 2-(2-thienyl)pyridine] (**4a**)	-2.29	0.40
[(N^C)Au(C≡CC_6H_4-4-F)$_2$] [N^C = 2-(5-methyl-2-thienyl)pyridine] (**5a**)	-2.48	0.55

Computational details

All calculations were performed with the Gaussian 03 program package[7] using the hybrid functional PBE1PBE[8] in conjunction with the Stuttgart/Dresden effective core potentials (SDD) basis set[9] for the Au center augmented with one f-polarization function (exponent α = 1.050) and the standard 6-31+G(d) basis set[10] for the remaining atoms. Full geometry optimizations without symmetry constraints were carried out in the gas phase for the singlet ground states (S_0) and the lowest triplet excited states (T_1). The optimized geometries were confirmed to be potential energy minima by vibrational frequency calculations at the same level of theory, as no imaginary frequency was found. The first 10 singlet-singlet and singlet-triplet transition energies were computed at the optimized S_0 geometries, by using the time-dependent DFT (TDDFT) methodology.[11] Solvent effects were taken into account using the conductor-like polarizable continuum model (CPCM)[12] with dichloromethane as solvent for single-point calculations on all optimized gas-phase geometries.

Energies and cartesian coordinates of the optimized ground-state structure of 1a

C	2.51684542	0.53873569	0.00774091	C	-2.03489815	5.97807543	-1.15646118
C	2.93047213	1.86956258	0.01898991	H	-2.14142787	6.53504152	-2.08423425
H	2.18538548	2.65992303	0.01850191	C	-2.47948090	6.53036873	0.04472991
C	4.28838240	2.19119291	0.03135191	C	-2.34100726	5.80615156	1.22889301
H	4.59429496	3.23483684	0.03983591	H	-2.68726507	6.22840379	2.16915708
C	5.25467696	1.18451034	0.03312891	C	-1.76320086	4.54104019	1.21594900
H	6.31135915	1.43813682	0.04273091	H	-1.65806615	3.97304510	2.13596407
C	4.86264824	-0.14841256	0.02294891	C	-1.21715168	-1.04887152	-0.01903409
H	5.62414793	-0.92439001	0.02498191	C	-2.30866205	-1.60196100	-0.01689009
C	3.50032197	-0.47674389	0.01046991	C	-3.58402948	-2.24392140	-0.01468609
C	3.01366023	-1.85756575	-0.00029509	C	-4.31482461	-2.39098304	-1.20663318
C	3.81166870	-3.00583725	0.00027291	H	-3.89725238	-2.00292522	-2.13146126
H	4.89160483	-2.91045779	0.01016191	C	-5.55649002	-3.01803945	-1.20057518
C	3.22012302	-4.26072003	-0.01197909	H	-6.11028513	-3.12147217	-2.13059825
H	3.84080561	-5.15284342	-0.01160509	C	-6.09297034	-3.50887321	-0.01012009
C	1.83053285	-4.36668033	-0.02491609	C	-5.37714021	-3.36603757	1.17859300
H	1.32922132	-5.32860317	-0.03555209	H	-5.79038541	-3.74168138	2.11159507
C	1.08260539	-3.20020186	-0.02427009	C	-4.13487577	-2.74015516	1.17980200
H	-0.00378069	-3.19521630	-0.03344909	H	-3.57825867	-2.62212043	2.10542407
C	-0.21055826	1.57074817	-0.00706009	N	1.66157006	-1.99210306	-0.01181909
C	-0.71626474	2.67947451	-0.00334009	Au	0.60859590	-0.18987839	-0.00943509
C	-1.31064112	3.97697891	0.01072791	H	-2.93265843	7.51838403	0.05762891
C	-1.45514575	4.71373205	-1.17738618	H	-7.06434265	-3.99688575	-0.00837509
H	-1.11073994	4.28053584	-2.11231025				

After PCM corrections, the SCF energy is -1228.831304 a.u.

Zero-point correction=	0.365468 (Hartree/Particle)
Thermal correction to Energy=	0.390171
Thermal correction to Enthalpy=	0.391115
Thermal correction to Gibbs Free Energy=	0.304170
Sum of electronic and zero-point Energies=	-1228.436482
Sum of electronic and thermal Energies=	-1228.411779
Sum of electronic and thermal Enthalpies=	-1228.410835
Sum of electronic and thermal Free Energies=	-1228.497780

Energies and cartesian coordinates of the optimized ground-state structure of 1b

C	-1.90720300	-2.12569700	-0.02591400	C	-2.60516000	-4.46853900	-0.03032500
C	-3.24914800	-1.75076500	-0.05177600	H	-2.36706700	-5.52933400	-0.02383800
H	-3.50773700	-0.69598700	-0.06484900	C	-1.58955200	-3.50322800	-0.01757900
C	-4.25701800	-2.71602500	-0.06513000	C	-0.16630300	-3.84562400	0.00224100
H	-5.29927700	-2.40602600	-0.08620700	C	0.36272200	-5.13986300	0.01959200
C	-3.93705500	-4.07411700	-0.05336800	H	-0.30527100	-5.99386400	0.01853700
H	-4.72378400	-4.82364300	-0.06397300	C	1.73728200	-5.32639000	0.03905800

H	2.14804200	-6.33242600	0.05260500	C	1.45733600	0.14391600	-0.00857900
C	2.58215900	-4.21784000	0.04182100	C	2.51104500	0.76566000	0.00478000
H	3.66193500	-4.32065500	0.05779100	C	3.74604700	1.48105300	0.02660400
C	2.01046400	-2.95582100	0.02472100	C	4.22880400	2.04215900	1.22204400
H	2.59781300	-2.04192200	0.02694400	H	3.64433700	1.93189800	2.13064800
C	-1.28441000	0.72659600	-0.01792800	C	5.43429000	2.73448900	1.25204900
C	-1.92875000	1.76085500	-0.01270800	H	5.81462600	3.17242800	2.16988800
C	-2.67424100	2.97711700	-0.01475900	C	6.15664500	2.86452700	0.07503800
C	-3.79176900	3.13854900	0.82234500	C	5.71444700	2.32992800	-1.12598600
H	-4.08384300	2.32422300	1.47910700	H	6.30884400	2.45918400	-2.02534800
C	-4.51818900	4.32429000	0.82461600	C	4.50754500	1.63932000	-1.14459200
H	-5.38113100	4.46107500	1.46912900	H	4.14004700	1.21701600	-2.07534600
C	-4.12034700	5.34900800	-0.02114900	N	0.68182200	-2.78406900	0.00454800
C	-3.02372600	5.23015400	-0.86233600	F	-4.82320600	6.50015300	-0.02520500
H	-2.74548600	6.05862100	-1.50653100	F	7.32746300	3.53395400	0.09872500
C	-2.30186200	4.04199300	-0.85363500	Au	-0.25748500	-0.92127400	-0.0132660
H	-1.43609500	3.92738500	-1.49890800				

After PCM corrections, the SCF energy is -1426.138640 a.u.

Zero-point correction=	0.349042	(Hartree/Particle)
Thermal correction to Energy=	0.375415	
Thermal correction to Enthalpy=	0.376359	
Thermal correction to Gibbs Free Energy=	0.284598	
Sum of electronic and zero-point Energies=	-1426.759912	
Sum of electronic and thermal Energies=	-1426.733540	
Sum of electronic and thermal Enthalpies=	-1426.732596	
Sum of electronic and thermal Free Energies=	-1426.824357	

Energies and cartesian coordinates of the optimized ground-state structure of 1e

C	-1.37557800	2.99484000	-0.03636800	H	-6.42765500	-2.76122600	-1.03681900
C	-2.76779000	2.94073500	-0.06615900	H	-6.27603300	-2.64158200	-2.79616100
H	-3.26224400	1.97390400	-0.08342900	H	-5.40243100	-3.90119300	-1.92319000
C	-3.52551500	4.11252000	-0.07581500	C	-4.09745400	-1.72936100	2.73724300
H	-4.61122100	4.05167000	-0.09872700	H	-3.33338200	-0.94258300	2.76938800
C	-2.90030000	5.35971800	-0.05632000	H	-4.81198000	-1.53116000	3.54917400
H	-3.49240800	6.27093900	-0.06355400	H	-3.60116200	-2.68001300	2.96308900
C	-1.51323700	5.43542800	-0.02884000	C	-5.59774100	-0.45292200	1.17585100
H	-1.03663300	6.41250400	-0.01567900	H	-6.19030700	-0.46242400	0.25327900
C	-0.74806900	4.26138300	-0.01939200	H	-6.29242600	-0.28336600	2.01098400
C	0.71586400	4.26604200	0.00539000	H	-4.92455300	0.41321200	1.13268600
C	1.52829300	5.40401200	0.02711400	C	-3.71806100	-4.87864500	0.60930200
H	1.07484900	6.38878900	0.02706100	H	-4.63838200	-4.95532300	0.01827800
C	2.90887200	5.26966900	0.04895200	H	-3.23282100	-5.86473000	0.58977400
H	3.53982000	6.15439600	0.06569700	H	-4.01139300	-4.68609100	1.64916000
C	3.47611700	3.99667200	0.04959200	C	-1.47058500	-3.77458500	0.90937100
H	4.55057300	3.84803300	0.06623100	H	-1.66244200	-3.52525700	1.96044900
C	2.62961000	2.89985800	0.02800300	H	-0.98739700	-4.76233200	0.89365700
H	2.99140600	1.87540300	0.02822000	H	-0.75597700	-3.03934000	0.52601400
C	-1.43279500	0.07601900	-0.03781500	C	4.13613200	-4.62940800	-1.15713600
C	-2.31318900	-0.77575600	-0.04245500	H	3.74605800	-5.15532700	-0.27663000
C	1.37768400	0.01126500	-0.02060200	H	4.02628000	-5.31011300	-2.01311100
C	2.29720400	-0.80477000	-0.03026700	H	5.20989700	-4.47561400	-0.99749400
N	1.29713200	3.03788400	0.00590500	C	1.89752600	-3.59939000	-1.68934100
Au	-0.04924600	1.43917800	-0.02217800	H	1.34198600	-2.68107100	-1.90582200
Si	-3.60505000	-2.08505300	-0.06280600	H	1.79093500	-4.27520900	-2.55003900
Si	3.66839600	-2.02979600	-0.02407700	H	1.40664100	-4.08152800	-0.83529100
C	-4.52031800	-1.91138600	-1.73088100	C	2.42872900	-3.51864900	2.08373400
H	-4.89795800	-0.87645900	-1.72997200	H	2.16969300	-4.32462600	1.38765200
C	-4.80898600	-1.75008200	1.38044300	H	2.49591500	-3.96156400	3.08780500
H	-5.52559600	-2.58743500	1.38323700	H	1.59306600	-2.80822600	2.09053900
C	-2.76365400	-3.79696500	0.08812000	C	4.11950600	-1.79464300	2.78213500
H	-2.48781900	-4.06452800	-0.94474200	H	3.38009400	-0.98465400	2.82808400
C	3.37733200	-3.32011500	-1.40717900	H	4.15314500	-2.26380500	3.77579200
H	3.79961300	-2.85805900	-2.31420600	H	5.10189900	-1.34165700	2.60145900
C	5.27431700	-1.03922400	-0.34645700	C	5.24888600	-0.30926600	-1.69246600
H	5.28196400	-0.27367800	0.44667300	H	4.34525300	0.30039300	-1.81355300
C	3.74107500	-2.82194200	1.71010200	H	6.12108700	0.35211800	-1.79918200
H	4.53559400	-3.58480000	1.67078000	H	5.28094200	-1.01577800	-2.53201400
C	-3.57590900	-2.05131700	-2.92826800	C	6.55390200	-1.86919000	-0.20676900
H	-3.17093600	-3.06899600	-3.00462200	H	6.62541500	-2.62885400	-0.99552000
H	-4.10535500	-1.84534400	-3.86949300	H	7.44614600	-1.23297300	-0.29588900
H	-2.72794300	-1.36019200	-2.86180200	H	6.61562100	-2.38687000	0.75827100
C	-5.72083300	-2.85217200	-1.87105200				

After PCM corrections, the SCF energy is -2055.182849 a.u.

Zero-point correction=	0.753400	(Hartree/Particle)
Thermal correction to Energy=	0.800488	
Thermal correction to Enthalpy=	0.801432	

Thermal correction to Gibbs Free Energy= 0.667558
Sum of electronic and zero-point Energies= -2054.412867
Sum of electronic and thermal Energies= -2054.365780
Sum of electronic and thermal Enthalpies= -2054.364836
Sum of electronic and thermal Free Energies= -2054.498710

Energies and cartesian coordinates of the optimized ground-state structure of 4a

C	6.00963500	-1.64139500	-1.09482800	C	-0.10147200	-3.57723100	0.03372400
C	4.62461900	-1.51603900	-1.09930500	H	0.92021600	-3.20743400	0.02930800
C	-1.57220100	4.81815100	0.22860000	Au	-0.70003800	-0.55938800	-0.00522500
C	-1.48305300	6.20557000	0.22545200	C	-0.40850600	4.01538000	-0.03449700
F	8.05670400	-1.32221600	0.04729500	F	-0.12470600	8.13184700	-0.04768700
C	6.71328700	-1.20241200	0.03754100	C	-0.21708700	6.78681600	-0.04345800
H	-5.96784200	0.38696200	-0.03119100	C	6.08142400	-0.64350200	1.15992000
S	-4.98586100	-1.84715700	-0.00065500	C	4.69611300	-0.52280300	1.14474000
C	-5.01386900	-0.12691000	-0.02223700	C	0.85508500	4.64510600	-0.30242000
H	-2.03656200	-6.35123300	0.06751700	C	0.95665300	6.03140700	-0.30791900
H	-3.79459600	-4.59048900	0.04090800	H	4.05410000	-1.84886300	-1.97725200
H	-3.57152100	1.49286400	-0.03963200	H	6.54434100	-2.06989500	-1.95334100
C	-3.75688100	0.42476100	-0.02640000	H	6.67099600	-0.30915100	2.02381100
C	-1.75730400	-5.30102100	0.05440800	H	4.18087100	-0.08324200	2.01035300
C	-2.74195200	-4.32421500	0.03957300	H	1.75867400	4.03122300	-0.50645900
H	0.38371100	-5.66486300	0.06227600	H	1.92667300	6.52828000	-0.51328200
C	-3.25399000	-1.83637100	0.00516200	H	-2.37513500	6.83543400	0.42726100
C	-0.41269200	-4.92861900	0.05151100	H	-2.55353700	4.34279400	0.43674200
C	-2.37178100	-2.97548800	0.02238900	C	1.30449700	-0.72055900	0.00007700
C	3.94441400	-0.95770600	0.01833800	C	2.52265700	-0.83039400	0.00843000
C	-2.73246800	-0.55447900	-0.01012700	C	-0.56912200	1.37560800	-0.02241300
N	-1.05150000	-2.63510500	0.01999000	C	-0.49785100	2.59182600	-0.03128300

After PCM corrections, the SCF energy is -1747.834458 a.u.

Zero-point correction= 0.315629 (Hartree/Particle)
Thermal correction to Energy= 0.341637
Thermal correction to Enthalpy= 0.342581
Thermal correction to Gibbs Free Energy= 0.251743
Sum of electronic and zero-point Energies= -1747.491834
Sum of electronic and thermal Energies= -1747.465825
Sum of electronic and thermal Enthalpies= -1747.464881
Sum of electronic and thermal Free Energies= -1747.555719

Energies and cartesian coordinates of the optimized triplet-state structure of 1a

C	-2.32931600	1.08097300	-0.02929900	C	2.79782600	5.78010300	0.72357300
C	-2.45092800	2.45406500	-0.06556300	H	2.58294700	6.65021200	1.33930800
H	-1.55217500	3.06397100	-0.08863600	C	3.94287700	5.75320300	-0.07260500
C	-3.71205800	3.07361900	-0.07671600	C	4.21200000	4.63046900	-0.85579800
H	-3.78776400	4.15680400	-0.10876900	H	5.10379100	4.60129900	-1.47720700
C	-4.90514500	2.28410800	-0.04764800	C	3.34632800	3.54191300	-0.84572000
H	-5.87104100	2.78291800	-0.05490200	H	3.55451500	2.66403800	-1.45067600
C	-4.84639900	0.92393200	-0.01259100	C	0.94133700	-1.28747800	0.00055900
H	-5.76221500	0.34111700	0.00799900	C	1.89274400	-2.05773700	0.00966000
C	-3.55952700	0.25841000	-0.00468300	C	3.01052900	-2.94396200	0.04001500
C	-3.39340800	-1.11979400	0.02476300	C	4.00509200	-2.79964300	1.02378500
C	-4.43866600	-2.10282500	0.05252500	H	3.91001100	-2.00068100	1.75358000
H	-5.47093700	-1.76900900	0.05080200	C	5.09304600	-3.66504800	1.05973000
C	-4.14399500	-3.43807900	0.08099900	H	5.85335500	-3.54012000	1.82692100
H	-4.93676000	-4.17960400	0.10274700	C	5.21327600	-4.68660400	0.11710000
C	-2.78220000	-3.84093100	0.08379500	C	4.23482800	-4.83610700	-0.86586800
H	-2.49861800	-4.88728500	0.11114200	H	4.32391800	-5.62677900	-1.60702400
C	-1.78320800	-2.86370100	0.05384400	C	3.14273000	-3.97550300	-0.90632300
H	-0.72788100	-3.12517300	0.05480600	H	2.38276700	-4.08678600	-1.67510700
C	0.54930000	1.48261500	-0.03613100	N	-2.04990700	-1.56627400	0.02530400
C	1.29889500	2.44400600	-0.03855900	Au	-0.64782400	-0.05209100	-0.01243500
C	2.18779200	3.56033700	-0.04955400	H	6.06578000	-5.36044300	0.14667000
C	1.92611700	4.69627500	0.73604000	H	4.62259200	6.60153800	-0.08150100
H	1.03592500	4.71338600	1.35903700				

After PCM corrections, the SCF energy is -1228.730047 a.u.

Zero-point correction= 0.360972 (Hartree/Particle)
Thermal correction to Energy= 0.386274
Thermal correction to Enthalpy= 0.387219
Thermal correction to Gibbs Free Energy= 0.298482
Sum of electronic and zero-point Energies= -1228.340705
Sum of electronic and thermal Energies= -1228.315403
Sum of electronic and thermal Enthalpies= -1228.314459
Sum of electronic and thermal Free Energies= -1228.403195

Energies and cartesian coordinates of the optimized triplet-state structure of 1b

C	-2.49087700	-1.37244100	-0.02414900
C	-3.62924500	-0.59632900	-0.05304500
H	-3.53134200	0.48547400	-0.06901800
C	-4.90934300	-1.17865100	-0.06602200
H	-5.79490700	-0.55005500	-0.09191600
C	-5.05591100	-2.60124000	-0.04654600
H	-6.05425300	-3.03130000	-0.05489700
C	-3.96697500	-3.41833800	-0.01951400
H	-4.09545900	-4.49625700	-0.00629100
C	-2.63538200	-2.84542500	-0.01068200
C	-1.46626200	-3.59235000	0.00816100
C	-1.37189200	-5.02468400	0.02223500
H	-2.28650700	-5.60785000	0.01863300
C	-0.15348300	-5.64598300	0.03985400
H	-0.08498600	-6.72954900	0.05086900
C	1.02285700	-4.85175800	0.04487300
H	2.01108000	-5.29794300	0.06178200
C	0.90349300	-3.45814800	0.02961300
H	1.77674900	-2.81039800	0.03326000
C	-0.97106600	1.10570000	-0.01569400
C	-1.23489200	2.29569100	-0.01218900
C	-1.52557900	3.69223800	-0.02067700
C	-2.58526300	4.21489400	0.74083500
H	-3.18441200	3.54166000	1.34716600
C	-2.86923000	5.57620700	0.73264700
H	-3.68362500	5.99056900	1.31907100
C	-2.08506500	6.41388600	-0.04651500
C	-1.02936100	5.93918200	-0.81086500
H	-0.43880000	6.63060000	-1.40411100
C	-0.75227700	4.57693600	-0.79280500
H	0.07203200	4.18251700	-1.37938100
C	1.41894500	-0.35376200	0.00168900
C	2.61698500	-0.10451000	0.01100600
C	4.01426500	0.18450300	0.03026300
C	4.61494400	0.73911000	1.17424700
H	3.99974500	0.94968700	2.04395200
C	5.97601400	1.02170600	1.20182500
H	6.44879900	1.45083600	2.07997900
C	6.73593100	0.74789000	0.07413500
C	6.18260700	0.20463700	-1.07583000
H	6.81280400	0.01009000	-1.93829100
C	4.82048000	-0.07520200	-1.09217800
H	4.36549700	-0.49582400	-1.98428000
N	-0.26706800	-2.83910700	0.01184000
F	-2.35762800	7.73497600	-0.06003600
F	8.05695400	1.02027700	0.09602100
Au	-0.54687800	-0.79377600	-0.00735800

After PCM corrections, the SCF energy is -1427.036733 a.u.

Zero-point correction=	0.344538 (Hartree/Particle)
Thermal correction to Energy=	0.371524
Thermal correction to Enthalpy=	0.372469
Thermal correction to Gibbs Free Energy=	0.279165
Sum of electronic and zero-point Energies=	-1426.663955
Sum of electronic and thermal Energies=	-1426.636968
Sum of electronic and thermal Enthalpies=	-1426.636024
Sum of electronic and thermal Free Energies=	-1426.729328

Energies and cartesian coordinates of the optimized triplet-state structure of 1e

C	-1.36029800	2.97407900	-0.03254300
C	-2.73768900	2.93425600	-0.06101400
H	-3.23757100	1.97002300	-0.08423100
C	-3.50209000	4.11410700	-0.06036100
H	-4.58692600	4.06124200	-0.08183600
C	-2.85886300	5.39209600	-0.02859200
H	-3.46812600	6.29242100	-0.02560800
C	-1.50136500	5.49353300	-0.00249000
H	-1.02993800	6.47132000	0.02110600
C	-0.68844700	4.29302900	-0.00813100
C	0.69943700	4.29135200	0.00490500
C	1.54965300	5.44759600	0.02560400
H	1.09361400	6.43190600	0.03066100
C	2.91082900	5.31594400	0.03854800
H	3.55195700	6.19204600	0.05400900
C	3.47402100	4.01256300	0.03154500
H	4.54715300	3.85647200	0.04179300
C	2.62344900	2.90268300	0.01059300
H	3.00965200	1.88622600	0.00534500
C	-1.42276800	0.06835100	-0.04117000
C	-2.30876200	-0.77810900	-0.04256600
C	1.38765000	0.01055600	-0.03767600
C	2.30495300	-0.80818900	-0.04885900
N	1.30352200	3.01098400	-0.00336200
Au	-0.03598700	1.43537100	-0.02948100
Si	-3.61056700	-2.07632400	-0.06331500
Si	3.66073800	-2.04917700	-0.02446800
C	-4.53749300	-1.87849800	-1.72273800
H	-4.90325800	-0.83922400	-1.71009600
C	-4.80428700	-1.74273900	1.39008400
H	-5.52681700	-2.57491200	1.39513500
C	-2.78701000	-3.79801100	0.06593300
H	-2.52118700	-4.06002500	-0.97083400
C	3.35496900	-3.37009900	-1.37678400
H	3.81207400	-2.95184700	-2.28815100
C	5.28117100	-1.09213200	-0.36800000
H	5.31552700	-0.32485500	0.42248400
C	3.71994300	-2.80868600	1.72548500
H	4.48376600	-3.60264200	1.69509500
C	-3.60361000	-2.01960400	-2.92796000
H	-3.21193900	-3.04160600	-3.01587500
H	-4.13642700	-1.79871000	-3.86388700
H	-2.74651300	-1.33999300	-2.86021900
C	-5.74980600	-2.80428800	-1.86079800
H	-6.44779400	-2.71467000	-1.01890200
H	-6.31189500	-2.57901100	-2.77836800
H	-5.44351100	-3.85614500	-1.92633800
C	-4.08342800	-1.73113100	2.74192800
H	-3.31280900	-0.95070500	2.77073600
H	-4.79039900	-1.53030500	3.55984500
H	-3.59266300	-2.68626100	2.96080100
C	-5.58620200	-0.44046700	1.19326400
H	-6.18491900	-0.44599200	0.27456900
H	-6.27416500	-0.26721600	2.03328300
H	-4.90774500	0.42146400	1.14627900
C	-3.74813500	-4.87410700	0.58621600
H	-4.67273800	-4.94023900	0.00070300
H	-3.27162800	-5.86427000	0.55803700
H	-4.03292300	-4.68522100	1.62905600
C	-1.48883900	-3.79563800	0.87941300
H	-1.67183500	-3.54893600	1.93270100
H	-1.01803400	-4.78918900	0.85591700
H	-0.76766000	-3.06713400	0.49596500
C	4.06377200	-4.69473600	-1.06810300
H	3.63859200	-5.17746800	-0.17915700
H	3.94840500	-5.39953000	-1.90364000
H	5.13863800	-4.57098700	-0.89078100
C	1.87275200	-3.60960600	-1.68018300
H	1.35447600	-2.68316500	-1.94849100
H	1.75942500	-4.31867500	-2.51285900
H	1.34781200	-4.03504100	-0.81644100
C	2.38434000	-3.44665000	2.12045100
H	2.08206900	-4.24418300	1.43210200
H	2.44512200	-3.88581500	3.12655600
H	1.58032100	-2.70070400	2.13196800
C	4.14610400	-1.77679300	2.77463200
H	3.43991100	-0.93698400	2.80916800
H	4.16765300	-2.22719000	3.77731300
H	5.14457500	-1.36727600	2.57877000
C	5.25704600	-0.36634400	-1.71626100
H	4.36964100	0.26849400	-1.82646000
H	6.14602100	0.26963100	-1.83746000
H	5.25683000	-1.07607200	-2.55380800
C	6.54178200	-1.95260500	-0.24079600
H	6.58377400	-2.71708600	-1.02708800
H	7.44813800	-1.33898800	-0.34469900
H	6.60351700	-2.46741000	0.72586100

After PCM corrections, the SCF energy is -2055.081668   a.u.

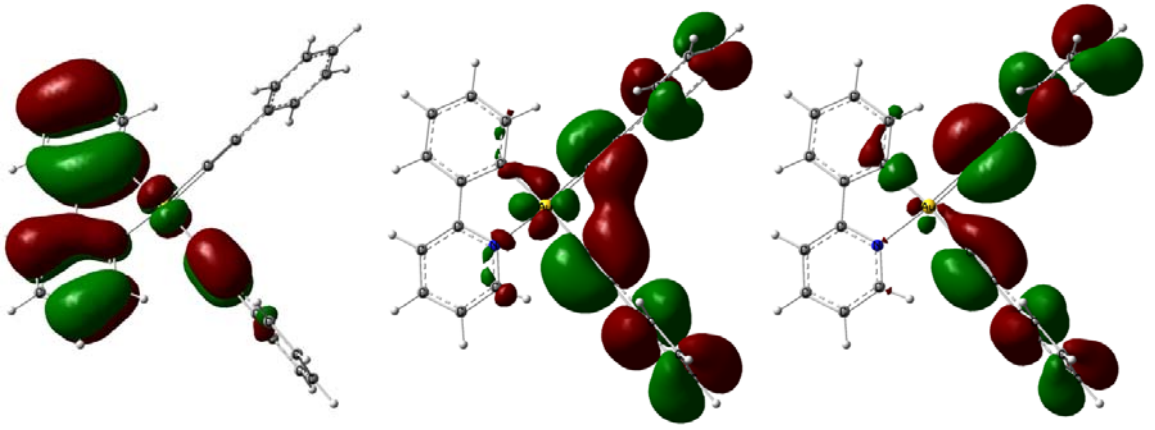
Zero-point correction=	0.749661 (Hartree/Particle)
Thermal correction to Energy=	0.797031
Thermal correction to Enthalpy=	0.797975
Thermal correction to Gibbs Free Energy=	0.664589
Sum of electronic and zero-point Energies=	-2054.316329
Sum of electronic and thermal Energies=	-2054.268959
Sum of electronic and thermal Enthalpies=	-2054.268014
Sum of electronic and thermal Free Energies=	-2054.401401

Energies and cartesian coordinates of the optimized triplet-state structure of 4a

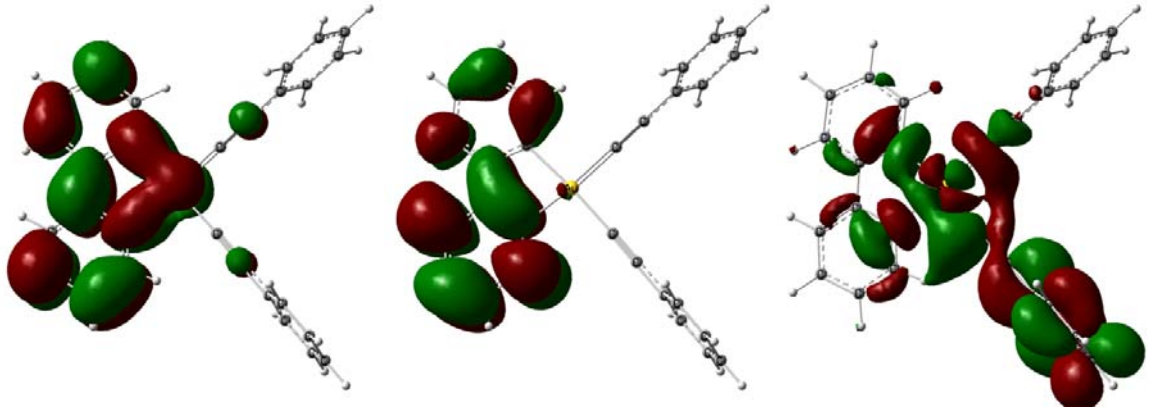
C	5.70742900	-2.26398800	-1.20693600	C	-0.82667800	-3.45571100	0.00013400
C	4.37815500	-1.85607100	-1.20481100	H	0.25027500	-3.30878100	-0.00246900
C	-0.52710100	5.04535700	0.04446900	Au	-0.80058300	-0.39464300	-0.00628500
C	-0.15243000	6.38416200	0.05310100	C	0.43693400	4.02352900	0.00240600
F	7.60661500	-2.94706000	0.00898100	F	1.56802500	7.99247400	0.02617100
C	6.31769100	-2.54951300	0.00549600	C	1.19884000	6.69552300	0.01825800
H	-5.76598800	1.58147600	-0.01380800	C	5.64708300	-2.43877300	1.21460600
S	-5.30123100	-0.85649500	-0.00320100	C	4.31805900	-2.02992100	1.20532400
C	-4.94312300	0.87699900	-0.01055400	C	1.79598900	4.38299200	-0.03191500
H	-3.27495300	-5.82655800	0.01009600	C	2.18255100	5.71826700	-0.02437100
H	-4.66247300	-3.76439900	0.00666300	H	3.88131500	-1.62362400	-2.14212700
H	-3.18669100	2.17217800	-0.01611400	H	6.27040100	-2.35998100	-2.13033900
C	-3.57134600	1.15781700	-0.01156300	H	6.16412600	-2.66816800	2.14137700
C	-2.80800200	-4.84610300	0.00687400	H	3.77503900	-1.93208100	2.14077700
C	-3.57760100	-3.70942900	0.00503000	H	2.54730500	3.59963100	-0.06432500
H	-0.75649300	-5.59822500	0.00493800	H	3.22893100	6.00667500	-0.05064200
C	-3.58704900	-1.19578900	-0.00237200	H	-0.88893300	7.18115100	0.08620500
C	-1.40007100	-4.72531700	0.00419300	H	-1.57999500	4.78022800	0.07188400
C	-2.95449000	-2.42916500	0.00076900	C	1.12656500	-0.95773700	-0.00766800
C	3.66066500	-1.73416300	-0.00181800	C	2.29555200	-1.31729300	-0.00645200
C	-2.76953300	0.03689500	-0.00707900	C	-0.27208900	1.47564900	-0.00732800
N	-1.55474500	-2.34221500	-0.00107200	C	0.05321900	2.64977800	-0.00500400

After PCM corrections, the SCF energy is -1747.750875   a.u.

Zero-point correction=	0.311962 (Hartree/Particle)
Thermal correction to Energy=	0.337584
Thermal correction to Enthalpy=	0.338528
Thermal correction to Gibbs Free Energy=	0.250152
Sum of electronic and zero-point Energies=	-1747.412256
Sum of electronic and thermal Energies=	-1747.386634
Sum of electronic and thermal Enthalpies=	-1747.385690
Sum of electronic and thermal Free Energies=	-1747.474067



HOMO -2 HOMO -1 HOMO



LUMO LUMO +1 LUMO +2

Energy (eV)		Composition (%)		
		ppy	Au	$(C{\equiv}CR)_2$
L+2	-1.00	16	25	59
L+1	-1.35	100	0	0
LUMO	-2.13	92	7	1
HOMO	-6.38	2	1	97
H-1	-6.46	2	5	93
H-2	-6.90	87	4	9

Figure S8. Spatial plots, energies (eV) and compositions (%) of selected frontier molecular orbitals of the ground-state of **1a**.

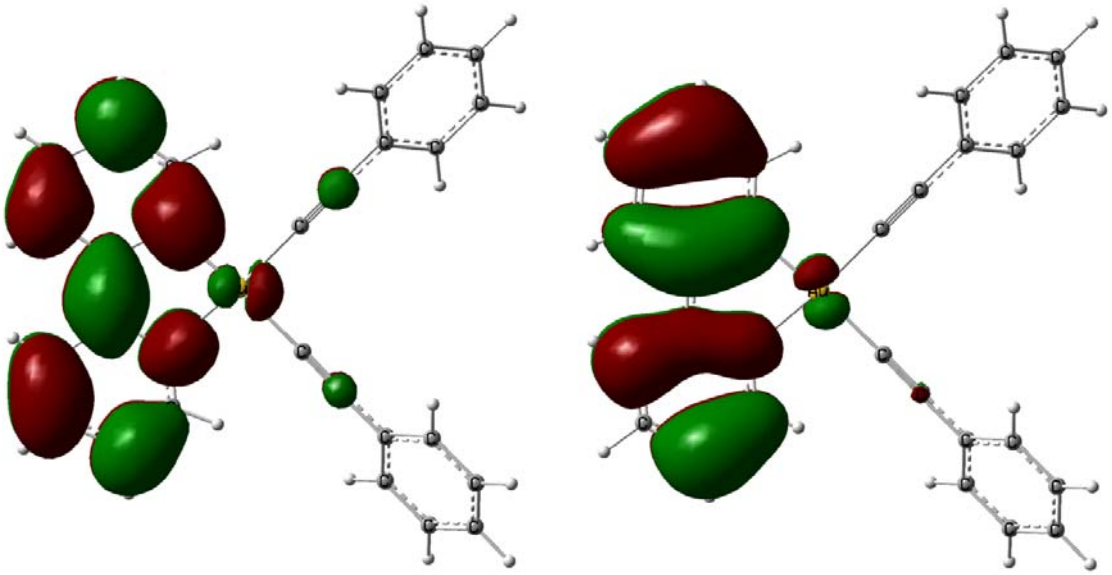


Figure S9. Singlet HOMO (top left) and singlet LUMO (top right) of the lowest triplet state of **1a**.

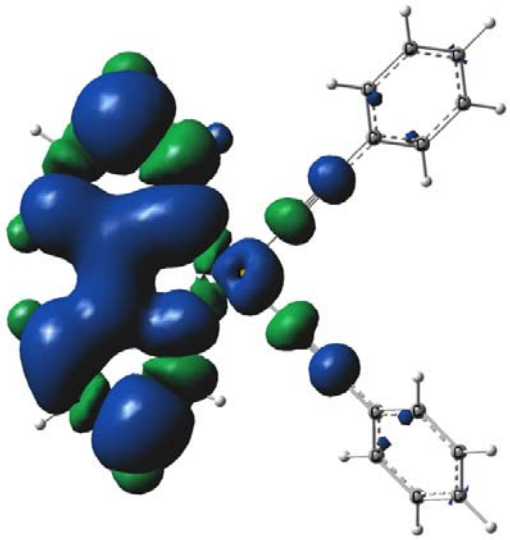
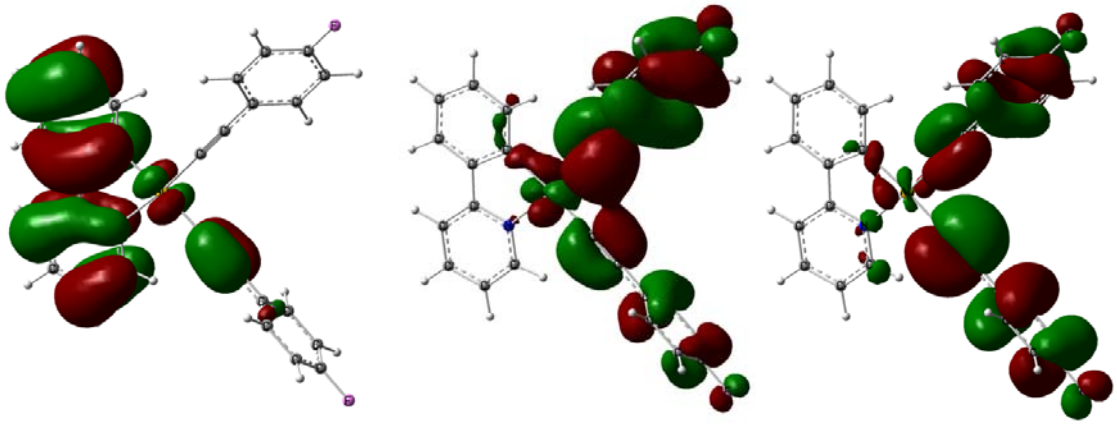
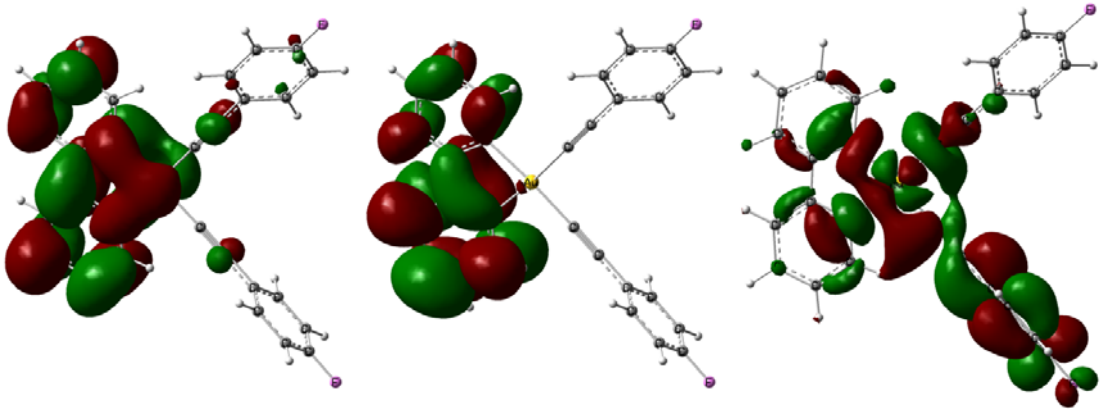


Figure S10. Triplet spin density surface of the lowest triplet state of **1a**.



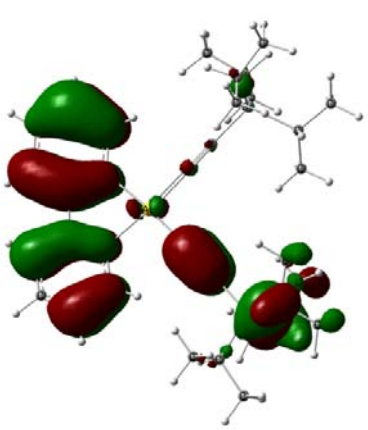
HOMO -2 HOMO -1 HOMO



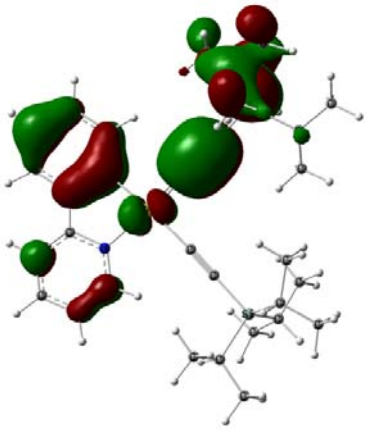
LUMO LUMO +1 LUMO +2

Energy (eV)		Composition (%)		
		ppy	Au	$(C{\equiv}CR)_2$
L+2	-1.01	22	28	50
L+1	-1.37	99	0	1
LUMO	-2.16	92	7	2
HOMO	-6.41	1	2	97
H-1	-6.46	1	5	94
H-2	-6.92	88	4	8

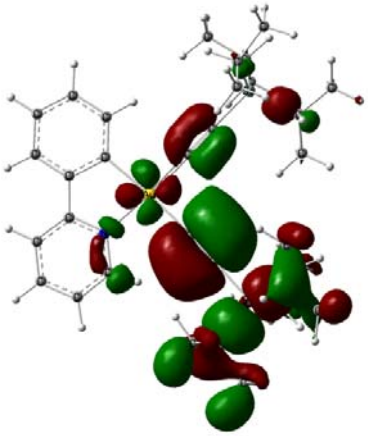
Figure S11. Spatial plots, energies (eV) and compositions (%) of selected frontier molecular orbitals of the ground-state of **1b**.



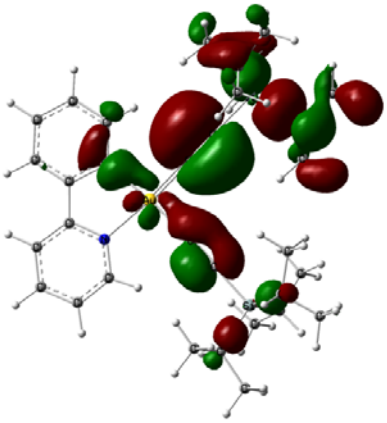
HOMO -4



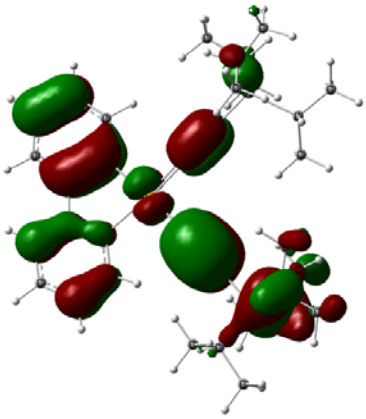
HOMO -3



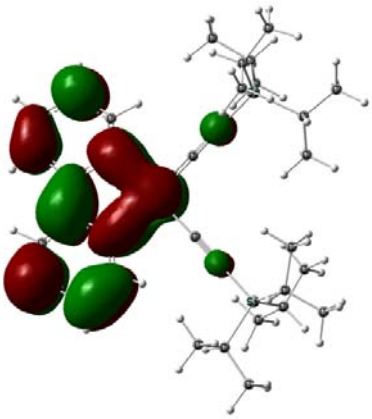
HOMO-2



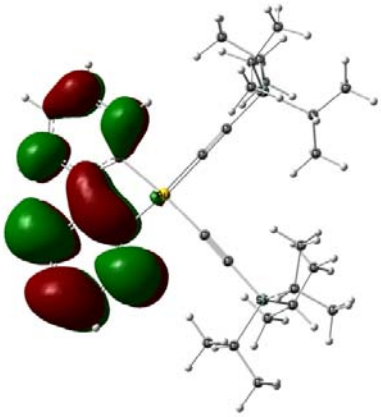
HOMO-1



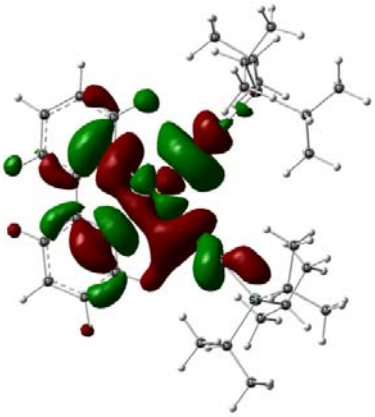
HOMO



LUMO



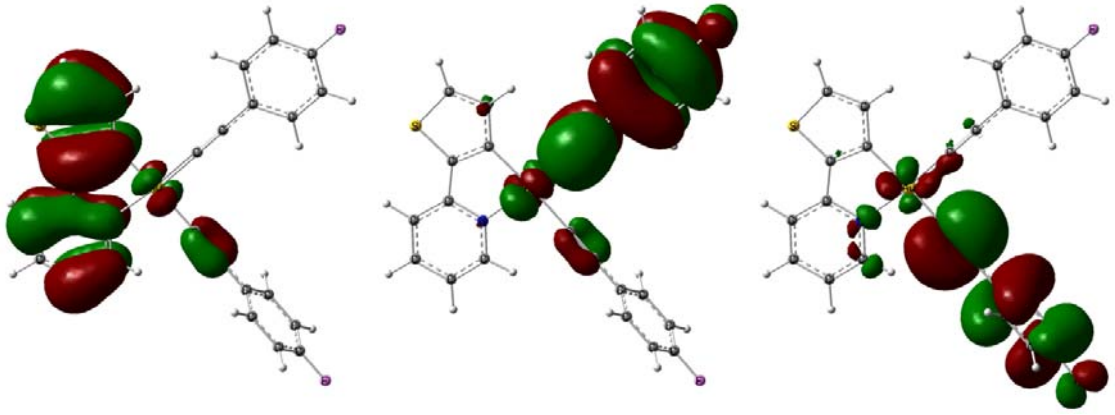
LUMO+1



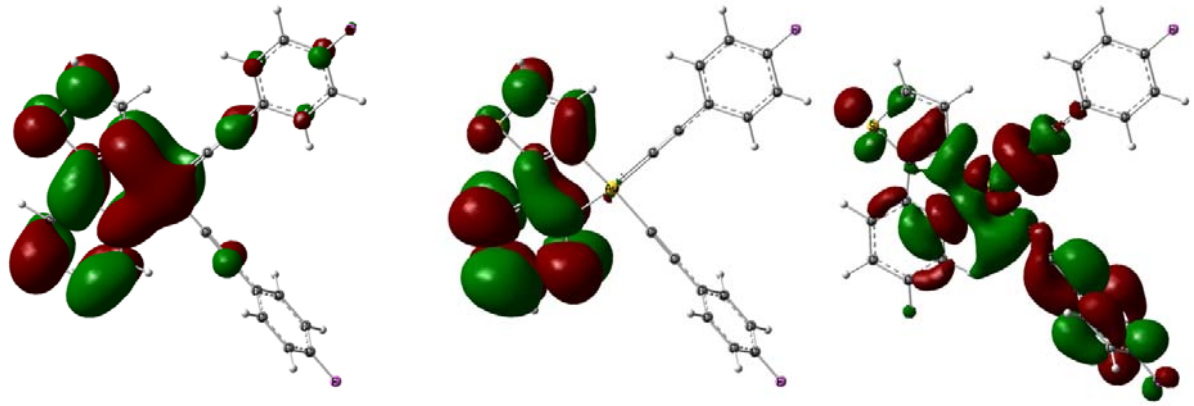
LUMO+2

Energy (eV)		Composition (%)		
		ppy	Au	$(C{\equiv}CR)_2$
L+2	-0.73	27	43	30
L+1	-1.35	100	0	0
LUMO	-2.12	92	7	1
HOMO	-6.75	28	6	66
H-1	-6.77	4	2	94
H-2	-6.86	1	5	94
H-3	-6.89	18	4	78
H-4	-7.01	67	1	32

Figure S12. Spatial plots, energies (eV) and compositions (%) of selected frontier molecular orbitals of the ground-state of **1e**.



HOMO -2 HOMO -1 HOMO



LUMO LUMO +1 LUMO +2

Orbital	Energy (eV)	MO composition (%)		
		thpy	Au	$(C{\equiv}CR)_2$
L+2	-1.13	25	30	45
L+1	-1.35	100	0	0
LUMO	-2.25	88	8	4
HOMO	-6.44	1	2	97
H-1	-6.54	2	4	94
H-2	-6.60	94	2	4

Figure S13. Spatial plots, energies (eV) and compositions (%) of selected frontier molecular orbitals of the ground-state of **4a**.

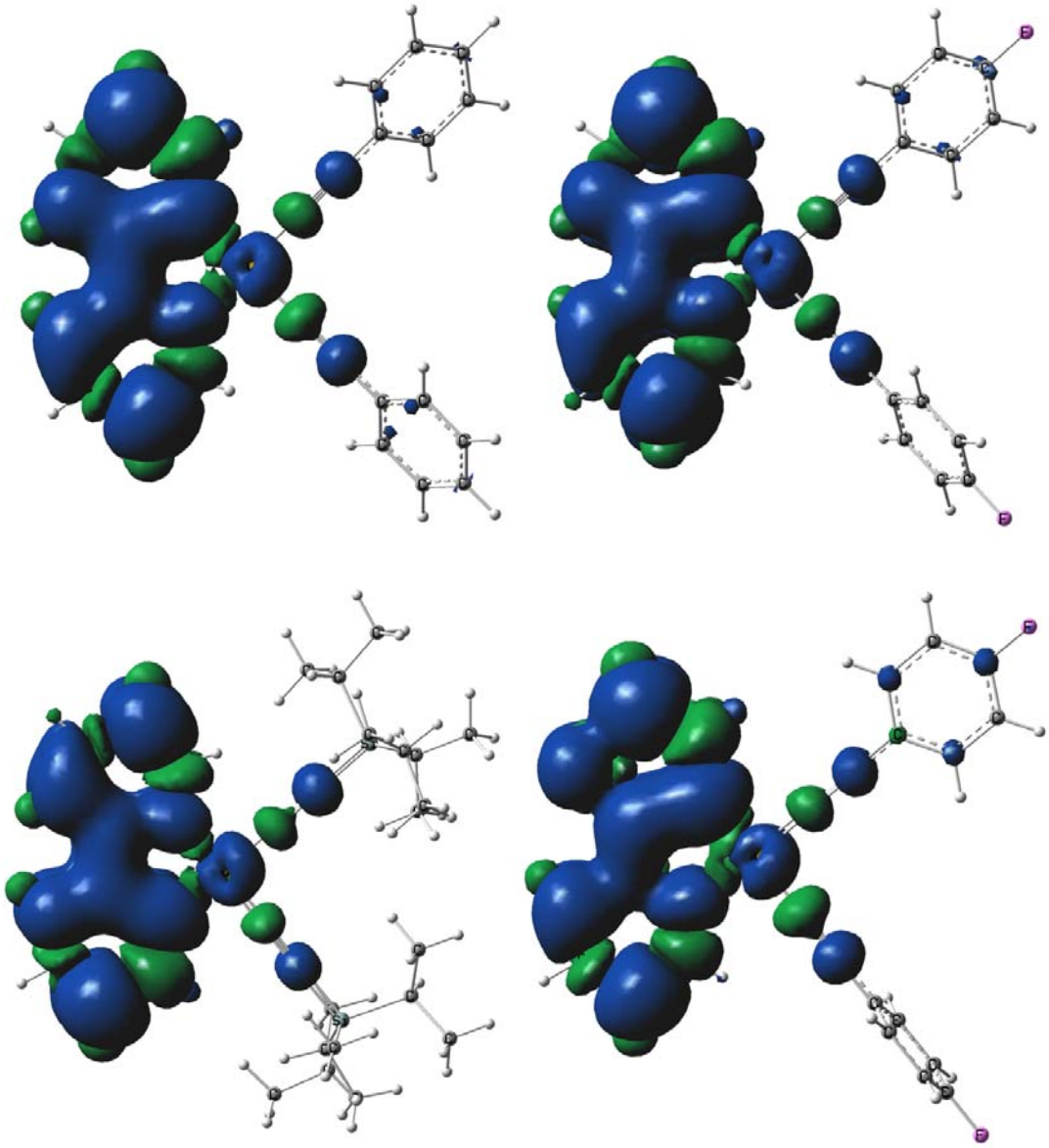


Figure S14. Triplet spin density surfaces of the lowest triplet state of **1a** (top left), **1b** (top right), **1e** (bottom left), and **4a** (bottom right).

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