Emissive biphenyl cyclometalated gold (III) diethyl dithiocarbamate complexes

Lakshmi Nilakantan,[†] David R. McMillin,[§]* and Paul R. Sharp[†]*

[†] 125 Chemistry, University of Missouri, Columbia, MO, 65211

[§] Department of Chemistry, Purdue University, West Lafayette, IN, 47907

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Experimental

1.1 Methodology to obtain lifetime and quantum yields for complexes 3a-d.

Lifetime. Emission lifetimes were determined by monitoring the entire emission spectrum at increasing delay time (t_d) ; the spectral shape remains constant with only a decrease in the overall intensity. The lifetime τ is obtained by calculating the slope of the line obtained by plotting the log of the integrated intensity against time. Details are given for **3a** with the same procedure followed for **3b-3d**. The lifetime was determined for frozen glass matrix (Figures S1-S4) and for the solid state using special cuvette at 298 K as well.

Quantum Yields. Quantum yields were determined as follows using **3a** as an example. Quinine sulfate (QS), which has a known quantum yield (ϕ) of 0.55 in water, was used as the standard. The first step in the quantum yield measurement is to obtain UV-Vis spectra. The UV-Vis spectrum was recorded for at least four solutions with increasing concentrations of **3a** and QS. The absorbance values were noted for an excitation wavelength of 287 nm for **3a** and QS. Then the emission spectrum for the same solutions (those used for UV-Vis measurements) of **3a** and QS were recorded by exciting at 287 nm. Next the emission spectra were corrected using manufactures supplied correction factors for instrument response. Finally the emission spectra were integrated from 300 to 530 nm, and then the integrated fluorescence intensity vs absorbance was plotted. The following equation was used to determine the quantum yield:

$\varphi_{x} = \varphi_{\text{STD}} \left[(\text{Slope}_{(x)} / \text{Slope}_{(\text{STD})} (\eta^{2}_{x} / \eta^{2}_{\text{STD}}) \right]$

where the subscripts X and STD refer to unknown and standard respectively, ϕ is the fluorescence quantum yield, the slope is obtained from the plot of integrated fluorescence intensity vs absorbance, η is the refractive index of the solvent. Here as an illustration, the plot of integrated fluorescence (FL) intensity vs absorbance of **3a** and QS are shown (Figure S11). The solvent used was dichloromethane (**3a**) and water (QS). By inserting the values of slope for **3a**, STD, $\phi_{STD} = 0.55$ and the refractive index of desired solvents the ϕ_{3a} is determined. The same procedure was followed to obtain quantum yields of **3b-3d**.

1.2. Table S1. UV-Vis data for 3a-d (2	298 K)) in CH ₂ Cl ₂
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complex	λ_{max} (nm)	$\epsilon (M^{-1} cm^{-1})$
3a	252	72300
	287	15570
	317	6660
	337	2070
3b ^a	248	79380
	287	18120
	316	7710
	337	2050
3c	259	106970
	297	23420
	306	22600
	340	7250
3d	256	71800
	287	19330
	307	8690
	320	6320

^a cyclohexane

1.3 Figures



Figure S1 Frozen glass emission spectra of **3a**, delay time ranges from 20 µs at highest intensity to 300 µs at lowest intensity, (glassing solvent 2-MeTHF).



Figure S2 Graph representing Log(integrated intensity) vs time of 3a at 77 K.



Figure S3 Solid state emission spectra of 3a, delay time ranges from 25 μ s at highest intensity to 80 μ s at lowest intensity



Figures S4 Plot of Log (integrated intensity) vs time of 3a (solid) at 298 K



Figure S5 Plot of Log (integrated intensity) vs time of **3b** at 77 K (glassing solvent 2-MeTHF).



Figure S6 Plot of Log(integrated intensity) vs time of 3b (solid) at 298 K



Figure S7 Plot of Log(integrated intensity) vs time of 3c at 77 K (glassing solvent 2-MeTHF).



Figure S8 Plot of Log(integrated intensity) vs time of 3c (solid) at 298 K



Figure S9 Plot of Log(integrated intensity) vs time of **3d** at 77 K (glassing solvent 2-MeTHF)



Figure S10 Plot of Log(integrated intensity) vs time of 3d (solid) at 298 K



Figure S11 Integrated Fluorescence intensity vs absorbance of 3a & QS



Figure S12. Photoemission intensity at room temperature and ~77 K for **3a** in 2-MeTHF (λ_{ex} = 365 nm, concentration = 3.4 x 10⁻³ M, 5 mm quartz tubes).



Figure S13. Photoemission intensity at room temperature of solid **3a**, **3b**, and **3d** ($\lambda_{ex} = 365 \text{ nm}$).



Figure S14. Photoemission spectra of **3a-d** in 2-methyltetrahydrofuran (2-MeTHF) glass (λ_{ex} (nm) = 337 (**3a**) concentration = 2.4 x 10⁻⁵ M, 334 (**3b**) concentration = 3.2 x 10⁻⁵ M, 336 (**3c**) concentration = 5.7 x 10⁻⁵ M, 346 (**3d**), concentration = 5.6 x 10⁻⁵ M). Intensities are arbitrary and set to minimize overlap.



Figure S15. Photoemission spectra of **3a-d** at room temperature in the solid state (λ_{ex} (nm) = 337 (**3a**), 334 (**3b**), 336 (**3c**), 346 (**3d**)). Intensities are arbitrary.



Figure S16. Photoemission spectra of **3b** at room temperature in various solvents ($\lambda_{ex} = 334$ nm, concentration = 1.7 x 10⁻⁵ M).



Figure S17 Excitation spectra in comparison with UV-Vis spectrum of **3b** at 298 K in degassed cyclohexane



Figure S18 Excitation spectra in comparison with UV-Vis spectrum of 3c at 298 K in degassed CH₂Cl₂



Figure S19 Excitation spectra in comparison with UV-Vis spectrum of 3d at 298 K in degassed CH_2Cl_2



Figure S20 Effect of aeration on the emission spectrum of 3a, 298 K in CH₂Cl₂.



Figure S21. ¹H NMR of compound **3a**. Solvent CD₂Cl₂. S: solvent I1: acetone I2: Petroleum ether w: water



Figure S22. ¹³C{¹H} NMR of compound 3a. Solvent CD_2Cl_2 .



Figure S23. ¹H NMR of compound 3b. Solvent CD₃COCD₃. S: solvent



Figure S24. ¹³C{¹H} NMR of compound **3b**. Solvent CD₃COCD₃.



Figure S25. ${}^{19}F{}^{1}H$ NMR of compound **3b**. Solvent CD₃COCD₃.



Figure S26. ¹H NMR of compound **3c**. Solvent CD₂Cl₂.



Figure S27. ¹³C{¹H} NMR of compound **3c**. Solvent CD_2Cl_2 .

Table S2. Comparison of bond lengths and angles between X-ray and from DFT studies for **3b**'-**3d**'

Bond length						
& Bond Angles	3b (Xray)	3b' (DFT)	3c (Xray)	3c' (DFT)	3d (Xray)	3d (DFT)
Au-C	2.030(4)	2.0456	2.025(2)	2.043	2.033(1)	2.0475
Au-C	2.033(4)	2.04564	2.026(2)	2.043	2.027(1)	2.0473
Au-S	2.3802(11)	2.5043	2.3968(5)	2.5175	2.3810(3)	2.5194
Au-S	2.3833(12)	2.5042	2.3968(5)	2.5172	2.3947(4)	2.5199
S-C	1.724(5)	1.7208	1.7349(18)	1.7194	1.732(1)	1.7195
Ph(C)-Ph(C)	1.478(6)	1.4631	1.485(4)	1.4632	1.470(2)	1.4602
C-Au-C	81.48(18)	80.557	80.80(12)	80.323	81.47(5)	80.4717
C-Au-S	176.65(12)	175.8215	176.86(6)	175.763	177.64(3)	175.6729
S-Au-S	74.80(4)	72.2027	74.56(3)	71.8663	74.61(1)	71.8083
S-C-S	113.6(3)	118.0737	113.61(18)	118.443	114.6(1)	118.4672



Figure S28 : Frontier orbitals of **3a**

Table S3: Major contributions MOs to the singlet and triplet transitions

Singlet	ts	
<mark>λ(nm)</mark>	OS	Major contribs (>6%)
388	0.0003	HOMO->LUMO (96%)
337	0.0231	HOMO->L+1 (86%), HOMO->L+2 (7%)
313	0.0006	H-1->LUMO (95%)
303	0	H-4->L+1 (10%), H-3->LUMO (87%)
299	0.0001	H-2->LUMO (95%)
297	0.0125	H-2->L+1 (18%), H-1->L+1 (71%)
296	0	H-4->L+1 (85%), H-3->LUMO (11%)
292	0.0132	HOMO->L+2 (76%), HOMO->L+1 (8%)
279	0.0004	HOMO->L+4 (39%), H-2->L+1 (35%), H-2->L+2 (8%), H-1->L+1 (7%)
268	0.0113	H-4->LUMO (10%), H-3->L+1 (78%)
260	0	HOMO->L+3 (88%)
259	0.0281	H-2->L+1 (34%), HOMO->L+4 (29%), H-1->L+1 (15%), H-2->L+2 (9%), H-5->LUMO (7%)
253	0.6416	H-4->LUMO (81%)
Triplet	s	
<mark>λ(nm)</mark>	OS	Major contribs (>6%)
457	-	HOMO->L+1 (24%), HOMO->L+2 (58%)
407	-	HOMO->LUMO (92%)



Figure S29 : Frontier orbitals of $\mathbf{3b}$

Table S4: Major contributions MOs to the singlet and triplet transitions in **3b**.

Singlet	ts	
<mark>λ(nm)</mark>	OS	Major contribs (>7%)
367	0.0003	HOMO->LUMO (95%)
325	0.0274	HOMO->L+1 (80%), HOMO->L+2 (8%)
317	0.0005	H-1->LUMO (98%)
298	0.0028	H-1->L+1 (86%)
296	0	H-3->LUMO (72%), H-4->L+1 (24%)
291	0	H-4->L+1 (68%), H-3->LUMO (25%)
290	0	H-2->LUMO (96%)
283	0.0091	HOMO->L+2 (54%), HOMO->L+3 (12%), H-2->L+1 (11%), HOMO->L+1 (8%)
277	0	HOMO->L+3 (41%), HOMO->L+2 (21%), H-2->L+1 (20%)
264	0.0004	H-3->L+1 (63%), H-4->LUMO (15%), HOMO->L+5 (12%)
253	0.6441	H-4->LUMO (75%)
Triplet	s	
<mark>λ(nm)</mark>	OS	Major contribs (>7%)
451	-	HOMO->L+2 (46%), HOMO->L+1 (32%)
383	-	HOMO->LUMO (91%)



Figure S30 : Frontier orbitals of **3c**

Singlets		
<mark>λ(nm)</mark>	OS	Major contribs (>7%)
407	0.0003	HOMO->LUMO (98%)
348	0.0026	HOMO->L+1 (92%)
342	0	H-1->LUMO (97%)
318	0	H-2->LUMO (98%)
308	0.0007	H-3->LUMO (98%)
303	0.0153	HOMO->L+2 (80%)
300	0.0819	H-1->L+1 (95%)
296	0.0135	H-3->L+1 (58%), H-4->L+1 (34%)
295	0.0078	H-4->L+1 (62%), H-3->L+1 (30%)
290	0.0057	H-2->L+1 (63%), HOMO->L+4 (16%)
271	0.0001	HOMO->L+3 (95%)
270	0.0462	HOMO->L+4 (39%), H-2->L+2 (29%), H-2->L+1 (28%)
269	0.0437	H-1->L+2 (85%)
253	0.6408	H-4->LUMO (89%)
Triplets		
<mark>λ(nm)</mark>	OS	Major contribs (>7%)
443	-	HOMO->L+2 (44%), HOMO->L+1 (20%), H-2->L+2 (15%)
432	-	HOMO->LUMO (97%)



Figure S31 : Frontier orbitals of **3d**

Table S6: Major contributions MOs to the singlet and triplet transitions in **3d**.

Singlets		
<mark>λ(nm)</mark>	OS	Major contribs (>7%)
405	0.0002	HOMO->LUMO (97%)
350	0.0419	HOMO->L+1 (90%)
315	0.0006	H-1->LUMO (95%)
305	0	H-3->LUMO (78%), H-4->L+1 (11%), HOMO->L+1 (9%), H-6->LUMO (8%), H-1- >L+1 (8%)
303	0.0781	HOMO->L+2 (71%)
301	0.0002	H-2->LUMO (88%)
298	0.0004	H-2->L+1 (30%), H-1->L+1 (55%), HOMO->L+2 (11%)
298	0	H-4->L+1 (82%), H-3->LUMO (13%)
283	0.0043	HOMO->L+4 (49%), H-2->L+1 (26%), H-1->L+1 (8%), H-1->L+2 (8%)
271	0	HOMO->L+3 (96%)
270	0.0049	H-3->L+1 (74%), H-4->LUMO (11%)
264	0.0735	H-2->L+1 (33%), H-1->L+1 (26%), HOMO->L+4 (26%)
256	0.6035	H-4->LUMO (81%)
Triplets		

<mark>λ(nm)</mark>	OS	Major contribs (>7%)
469	-	HOMO->L+2 (59%), HOMO->L+1 (24%)
423	-	HOMO->LUMO (93%)



Figure S32: Structure of triplet ^{T1}**3b'** with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.03, blue font) and selected distances (black font). (Lower half of the molecule is identical to the upper half. Au = yellow, S = red, N = blue, C = grey, H = white).

Description: The structure of this triplet (^{T1}**3b'**) is shown in Figure S32 As in **3a'**, with the exception of the fluorine atoms the molecule is planar with C_{2v} symmetry. The character of the triplet is revealed by the spin density surfaces, atomic spin values, and selected distances shown in the figure. Consistent with bph π - π * (HOMO->LUMO+2) character, spin density is localized in the bph-ligand π system with only a small amount on the Au atom. In addition, population of the predominantly bph π * LUMO+2 orbital is evident from the C1-C1' distance reduction from 1.46 A in **3b'** to 1.38 A in ^{T1}**3b'**. The lack of involvement of the Au-ligand antibonding LUMO is apparent from the Au-ligand distances which change little (<0.02 A) from those in **3b'**.



Figure S33. Structure of triplet ^{T2}**3a'** a) with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.01, blue font) and selected distances (black font) and b) side view showing slight "twist". (Au = yellow, S = red, N = blue, C = grey, H = white).

Description: A planar triplet structure (**TS22a**') similar to ^{T1}**3b**' was obtained from **3a**' (Figure S42). However, **TS22a'** is a transition state connecting two enantiomeric non-planar "twisted" triplet structures ^{T2}**3a'** (Figure S37). The twist of ~10° is along the dtc-Au-bph axis and reduces the symmetry to C₂. Spin density and bond distances indicate contributions from the Au-ligand antibonding LUMO and the HOMO. A slight reduction in the C1-C1' distance from 1.48 Å in **3a'** to 1.42 Å is consistent with partial depopulation of the HOMO, which is antibonding with respect to the C1-C1' interaction. Partial population of the LUMO results in an increase in the Au-ligand distances from 2.05 (Au-C) and 2.50 Å (Au-S) in 3a' to 2.12 and 2.60 Å in ^{T2}**3a'**. A similar triplet structure (^{T2}**3d'**) was located for **3d'** (Figure S34).



Figure S34 Structure of triplet ^{T2}3d' with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances (black font). The structure is C_2 symmetric.



Figure S35. Structure of triplet ${}^{T3}3a$, a) with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances and b) side view showing distorted coordination.

Description. Other low-energy triplet structures were located for 3a'-3d'. These are more distorted structures than ^{T2}3a' and are non-planar with strongly different Au-S and Au-C distances. The first of these (^{T3}3a') is shown in Figure S35. While the distortion from 3a' makes correlation of ^{T3}3a' with 3a' orbital occupancy more difficult, the spin density and distances again suggest that this triplet is derived from partial population of the LUMO of 3a'. Some contribution from the π system is also present. Similar triplet structures (^{T3}3c' and ^{T3}3d', Figures S36-S37) were located for 3c' and 3d' but not for 3b'.



Figure S36 Structure of triplet ^{T3}3c' with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances (black font).



Figure S37 Structure of triplet ^{T3}3d' with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances (black font).



Figure S38. Structure of triplet ^{T4}**3a'** a) with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances and b) side view showing distorted coordination.

Description : All four model complexes yielded more severely distorted triplet structures $^{T4}3a'$ -^{T4}3d'. The structure for $^{T4}3a'$ is given in Figure S38 while those for $^{T4}3b'$ - $^{T4}3d'$ can be found in Figures S39-S41. The spin-density distribution in $^{T4}3a'$ is similar to that in $^{T3}3a'$ and a comparison of the geometries suggests that $^{T4}3a'$ is a rotamer of $^{T3}3a'$. Either rotation of the bph ligand around the short Au-C2 bonding axis by ~90° or a similar rotation of the dtc ligand in $^{T3}3a'$ would yield the essential geometry of $^{T4}3a'$. A transition state structure (TS33c') (Figure S45) connecting $^{T3}3c'$ with its enantiomer is located 0.9 kcal/mol above $^{T3}3c'$ (Table S7).



Figure S39. Structure of triplet ^{T4}**3b'** with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances (black font).



Figure S40. Structure of triplet ^{T4}3c' with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances (black font).



Figure S41 Structure of triplet ^{T4}3d' with Mulliken spin density surfaces (isovalue = 0.004) and atomic spin values (|value| > 0.02, blue font) and selected distances (black font).



Figure S42. Structure of transition state **TS22a'**.



Figure S43. Structure of transition state **TS23a**'.



Figure S44. Structure of transition state **TS14b'**.



Figure S45. Structure of transition state **TS33c'**.



Figure S46. Structure of transition state **TS34a'**.



Figure S47. MECP structure for a) **3a'**, b) **3b'**, c) **3c'**, and d) **3d'** (distances in Angstroms).

Table S7. Triplet transition state free energies (kcal/mol, gas phase) relative to ground state 3x' (x = a, b, c) and connected triplets. (The first two digits in the transition-state labels indicate the connected triplet structures.)

Relative to	TS22a'	TS23a'	TS34a'	TS14b'	TS33c'
Singlet	61.0	58.7	58.5	51.6	57.7
1 st /2 nd Triplet	2.9/2.9	0.6/0.9	0.8/2.6	3.9/5.4	0.9/1.2