Supporting Information

Enhancement of the Luminescent Efficiency in Carbene-Au⁽¹⁾-Aryl Complexes by the Restriction of Renner-Teller Distortion and Bond Rotation

Tian-yi Li, Daniel Sylvinson Muthiah Ravinson, Ralf Haiges, Peter I. Djurovich, Mark E. Thompson Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States

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Synthesis and characterization Synthesis of 4-(dimethylamino)-2,6-dimethylphenyl boronic acid



N,*N*,3,5-tetramethyl aniline (1.0 g, 1.1 mL, 6.7 mmol) was dissolved in 15 mL anhydrous MeCN, and a 15 mL MeCN solution of 1.19 g *N*-Bromosuccinimide (NBS, 6.7 mmol) was added with vigorous stirring at 0 °C. Then the mixture was allowed to RT and stirred overnight. The volatiles were then removed under vacuum. The oily residue was taken up into excess amount of DCM and washed with brine. The organic phase was collected and flash column chromatography (silica, eluent DCM:hexane = 1:1 v/v) provided the final product as colorless oil which turned into white fine crystalline (1.2 g, yield: 79%) upon cooling down to ~10 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.47 (s, 2H, Ar*H*), 2.90 (s, 6H, N(C*H*₃)₂), 2.38 (s, 6H, ArC*H*₃).



4-bromo-*N*,*N*,3,5-tetramethylaniline (0.5 g, 2.2 mmol, 1 equiv.) was dissolved in 50 mL anhydrous THF. After cooling the solution down to -78 °C, 2.2 mL n-BuLi (2.5 M in toluene, 2.5 equiv.) was added dropwise. Then, the mixture was warmed up to RT gradually and stirred at RT for 1 h. The solution was cooled down to -78 °C again. Upon the addition of 1.0 mL freshly stilled trimethyl borate (8.8 mmol, 4 equiv.) dropwise, the reaction system was stirred at RT overnight. The reaction was quenched by the addition of 20 mL 1.5 M HCl solution and the aqueous phase was washed by diethyl ether. After the neutralization of the aqueous phase, the organic product was taken up with diethyl ether. The final product was crashed out as white powder by the addition of excess amount of hexane into a concentrated diethyl ether solution. ¹H NMR (400 MHz, DMSO) δ 7.83 (s, 2H, Ar*H*), 6.31 (s, 2H, B(O*H*)₂), 2.80 (s, 6H, N(C*H*₃)₂), 2.19 (s, 6H, ArC*H*₃). *Note, the obtained boronic acid degrades gradually even under inert atmosphere*. Thus, it was used in the following reactions immediately.

Synthesis of 4-(3,5-dimethyl)-julolidine boronic acid pinacol ester



An oven-dried flask was charged with 1.54 mL 3,5-dimethyl aniline (1.5 g, 12.4 mmol, 1 equiv.), 26.9 mL 1-bromo-3-chloropropane (42.9 g, 272 mmol, 22 equiv.) and 5.5 g anhydrous Na_2CO_3 (52 mmol, 4.2 equiv.). The mixture was heated at 80 °C for 2 h with vigorous stirring. Then, the reaction temperature was increased to 90 °C for another 2 h and kept at 120 °C overnight. After removing the excess amount of

1-bromo-3-chloropropane under reduced pressure, the raw product was taken up into DCM and washed by brine. The organic phase was collected, and flash column chromatography provided the final product as colorless oil that turned into white crystalline (2.0 g, yield 80%) upon cooling down to ~10 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.39 (s, 1H, Ar*H*), 3.07 (td, J = 5.6, 1.4 Hz, 4H, NC*H*₂CH₂), 2.64 (t, *J* = 6.8 Hz, 4H, ArC*H*₂CH₂), 2.13 (s, 6H, ArC*H*₃), 2.07 – 1.98 (m, 4H, CH₂C*H*₂CH₂).



A MeCN solution of NBS (1.77 g, 9.9 mmol, 1 equiv.) was added dropwise into a MeCN solution of 3,5-dimethyljulolidine (2.0 g, 9.9 mmol, 1 equiv.) at 0 °C. The resultant suspension was stirred vigorously overnight. After removing all the volatiles under reduced pressure, the residual solid was dissolved in excess amount of DCM and washed by brine. The organic phase was collected and flash chromatography (silica, eluent DCM:hexane = 1:1 v/v) provided the final product as white crystalline powder (2.1 g, yield 75%). ¹H NMR (400 MHz, CDCl₃) δ 3.08 – 2.98 (m, 4H, NC*H*₂CH₂), 2.69 (t, *J* = 6.8 Hz, 4H, ArC*H*₂CH₂), 2.31 (s, 6H, ArC*H*₃), 2.05 – 1.93 (m, 4H, CH₂CH₂).



An oven-dried flask was charged with 4-bromo-3,5-dimethyl julolidine (0.5 g, 1.8 mmol, 1 equiv.), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.9 g, 0.88 mL, 7.2 mmol, 4 equiv.) and triethyl amine (0.72 g, 1.0 mL, 7.2 mmol, 4 equiv.) in 40 mL anhydrous THF and 0.09 g Mg (3.6 mmol, 2 equiv.) that was treated by 0.5 M HCl and dried completely was suspended in the solution. The mixture was heated at reflux overnight. After cooling down to RT, the reaction was quenched by the addition of brine. The organic raw product was taken up into DCM, flash chromatography (silica, eluent hexane:ethyl acetate = 10:1 v/v) provided the final product as white powder (0.45 g, yield 77%). ¹H NMR (400 MHz, CDCl₃) δ 3.08 – 2.97 (m, 4H, NCH₂CH₂), 2.59 (t, J = 6.7 Hz, 4H, ArCH₂CH₂), 2.18 (s, 6H, ArCH₃), 2.03 – 1.92 (m, 4H, CH₂CH₂), 1.36 (s, 12H, C(CH₃)₂).

X-ray crystallographic section

The structures of 1a, 1b, 1c, 2a, 2b, 2d, 2d-Me and 2e-Me were determined by single crystal X-ray crystallographic measurements. Refinement of disorder on diisopropyl moieties are carried out in 1a and 2d, and structural disorder of the MAC carbene ligand is refined in 2a and 2d. The details of data collection and solution are given below and cif files are provided as supplementary materials.



Thermal ellipsoids shown at 50% probability and hydrogens are removed for clarity.

<u>1a</u>					
C1-Au	2.0228	(31) Å			
Au-C2	2.0257	(33) Å			
C1-C2	4.0452	(45) Å			
N1-C1-N2	117.2(3)°				
N1-C1-Au	121.0(2)°	∑=359.9°			
N2-C1-Au	121.7(2)°	-			
C1-Au-C2	175.37	/(11)°			
C3-C2-C4	115.8(4)°	· ·			
C3-C2-Au	122.2(3)°	Σ =359.8°			
C4-C2-Au	121.8(3)°	-			
Dihedral angle (NHC-Phenyl)	17.571	.(96)°			
1b		~ /			
C1-Au	2.0133(130) Å			
Au-C2	2.0193(143) Å			
C1-C2	4.0321(194) Å			
C5-N3	1.4293(173) Å			
N1-C1-N2	116.7(11)°				
N1-C1-Au	121.4(9)°	Σ=359.9°			
N2-C1-Au	121.8(9)°				
C1-Au-C2	178.3	6(5)°			
C3-C2-C4	116.5(13)°				
C3-C2-Au	121.9(10)°	$\Sigma = 359.9^{\circ}$			
C4-C2-Au	121.5(11)°				
C5-N3-C6	126.3(12)°				
C5-N3-C7	125.7(12)°	Σ=359.9°			
C6-N3-C7	107.9(11)°				
Dihedral angle (NHC-Phenyl)	2.737(442)°			
Dihedral angle (Phenyl-Carbazolyl)	48.757	(387)°			
1c		()			
C1-Au	2.0169	(16) Å			
Au-C2	2.0180	(17) Å			
C1-C2	4.0345	(24) Å			
C5-N3	1.4163	(22) Å			
N1-C1-N2	117.39(15)°				
N1-C1-Au	122.71(12)°	$\Sigma = 360.0^{\circ}$			
N2-C1-Au	119.88(12)°				
C1-Au-C2	178.3	3(6)°			
C3-C2-C4	115.16(16)°	~ (*)			
C3-C2-Au	120.73(13)°	Σ=360 0°			
C4-C2-Au	124.08(13)°	L 200.0			
C5-N3-C6	119.78(15)°				
C5-N3-C7	120,12(15)°	Σ=359 5°			
C6-N3-C7	119.63(15)°	L 337.3			

 Table S1. Selected bond lengths and angles of the single crystal structures

Dihedral angle (NHC-Phenyl)	e (NHC-Phenyl) 51.972(53)°		
Dihedral angle (Phenyl-Diphenylamino)	o) 34.187(121)°		
2a		· · ·	
C1-Au	2.0370	(34) Å	
Au-C2	2.0272	(41) Å	
C1-C2	4.0632	(53) Å	
N1-C1-N2	117.0(3)°		
N1-C1-Au	121.0(2)°	Σ=360.0°	
N2-C1-Au	122.0(3)°		
C1-Au-C2	177.36	6(14)°	
C3-C2-C4	115.5(4)°		
C3-C2-Au	121.1(3)°	Σ=360.0°	
C4-C2-Au	123.4(3)°		
Dihedral angle (NHC-Phenyl)	13.294	(117)°	
2b		\$ 2	
C1-Au	2.0628(120) Å	
Au-C2	2.0471(130) Å	
C1-C2	4.1078(178) Å	
C5-N3	1.4397(170) Å	
N1-C1-N2	118.6(11)°		
N1-C1-Au	121.1(9)°	∑=359.9°	
N2-C1-Au	120.2(9)°	_	
C1-Au-C2	176.3	B(5)°	
C3-C2-C4	116.6(12)°		
C3-C2-Au	121.7(10)°	Σ =360.0°	
C4-C2-Au	121.7(10)°	_	
C5-N3-C6	125.0(11)°		
C5-N3-C7	126.3(12)°	∑=359.7°	
C6-N3-C7	108.4(12)°		
Dihedral angle (NHC-Phenyl)	4.124((316)°	
Dihedral angle (Phenyl-Carbazolyl)	52.601	(344)°	
2d			
C1-Au	2.0233	(48) Å	
Au-C2	2.0361	(71) Å	
C1-C2	4.0594	(86) Å	
C5-N3	1.393(12) Å	
N1-C1-N2	114.431(629)°		
N1-C1-Au	122.785(495)°	∑=360.0°	
N2-C1-Au	122.7(5)°		
C1-Au-C2	180.	00°	
C3-C2-C4	115.1(6)°		
C3-C2-Au	122.5(3)°	∑=360.0°	
C4-C2-Au	122.5(3)°		
C5-N3-C6	119.5(5)°	$\nabla - 260.09$	
C5-N3-C7	119.5(5)°	$\Sigma = 300.0^{\circ}$	

C6-N3-C7	121.1(10)°			
Dihedral angle (NHC-Phenyl)	62.452	(367)°		
Dihedral angle (Phenyl-Dimetylamino)	10.259	(269)°		
2d-Me				
C1-Au	2.0397	(22) Å		
Au-C2	2.0440	(22) Å		
C1-C2	4.0836	(31) Å		
C5-N3	1.421	(3) Å		
N1-C1-N2	116.3(2)°	· · /		
N1-C1-Au	121.07(16)°	Σ =359.9°		
N2-C1-Au	122.51(17)°	-		
C1-Au-C2	179.1	7(9)°		
C3-C2-C4	116.2(2)°			
C3-C2-Au	122.00(17)°	∑=360.0°		
C4-C2-Au	121.76(17)°	-		
C5-N3-C6	116.7(2)°			
C5-N3-C7	116.1(2)°	∑=360.0°		
C6-N3-C7	112.2(2)°	-		
Dihedral angle (NHC-Phenyl)	6.212	(85)°		
Dihedral angle (Phenyl-Dimetylamino)	37.996	(160)°		
2e-Me				
C1-Au	2.0344	(27) Å		
Au-C2	2.0505	(26) Å		
C1-C2	4.0806	(37) Å		
C5-N3	1.4174	(35) Å		
N1-C1-N2	116.4(2)°			
N1-C1-Au	120.8(2)°	∑=360.0°		
N2-C1-Au	122.76(19)°			
C1-Au-C2	174.73	(10)°		
C3-C2-C4	117.3(2)°			
C3-C2-Au	120.7(2)°	∑=359.6°		
C4-C2-Au	121.6(2)°			
C5-N3-C6	116.1(2)°			
C5-N3-C7	116.0(2)°	∑=344.9°		
C6-N3-C7	112.8(2)°			
Dihedral angle (NHC-Julolidine) 21.835(53)°				
The numbering system of the molecules is based on Figure S1. The dihedral angles are determined by				
measuring the dihedral angle between the two planes gener	ated through all the atoms	in that plane.		

Complex	1a	1b	1c	2a	2b	
Formula	C ₃₆ H ₄₅ AuN ₂ O	C48H52AuN3O	C48H54AuN3O	C ₃₆ H ₄₇ AuN ₂	C48H54AuN3	
	2	2	2	0	0	
Formula weight	734.70	899.89	901.91	720.72	885.91	
Temperature	100 K	100 K	100 K	100 K	100 K	
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	
Crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic	
Space group	$P2_1/c$	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	ΡĪ	
a (Å)	10.1743(14)	11.018(7)	11.380(2)	10.233(3)	11.072(3)	
b (Å)	17.827(3)	14.238(9)	14.959(3)	17.846(4)	15.898(4)	
<i>c</i> (Å)	18.078(3)	14.308(9)	15.152(3)	17.766(4)	24.215(6)	
α (deg)	90	113.992(8)	98.414(3)	90	90.721(4)	
β (deg)	90.286(2)	98.581(11)	102.154(3)	93.463(4)	94.132(4)	
γ (deg)	90	95.042(9)	101.174(3)	90	102.353(4)	
Volume (Å ³)	3278.9(8)	2000(2)	2426.1(8)	3238.4(13)	4151.0(18)	
Ζ	4	2	2	4	4	
F (000)	1480.0	912.0	916.0	1456.0	1800.0	
θ (deg) for collection	2.30 to 30.53	2.26 to 26.47	2.58 to 31.28	2.28 to 30.52	2.44 to 24.43	
Index range	-12<=h<=12	-13<=h<=13	-14<=h<=14	-12<=h<=12	-12<=h<=12	
	-21<=k<=21	-17<=k<=17	-18<=k<=18	-22<=k<=22	-18<=k<=8	
	-22<=l<=22	-17<=l<=17	-18<=l<=18	-21<=l<=21	-27<=l<=27	
Reflections collected	57714	27321	45460	58135	63253	
Unique (R_{int})	9730 (0.0430)	6800 (0.0907)	9640 (0.0397)	9779	9832	
				(0.0421)	(0.0471)	
data/restrain/paramete	6452/0/401	7837/0/497	9524/0/497	6356/0/381	13108/0/975	
r						
Goodness of Fit	1.037	1.019	1.009	1.049	1.035	
Final <i>R</i> indices	$R_1 = 0.0275$	$R_1 = 0.0967$	$R_1 = 0.0162$	$R_1 = 0.0256$	$R_1 = 0.0687$	
$[I > 2\sigma(\mathbf{I})]$	$wR_2 = 0.0732$	$wR_2 = 0.2614$	$wR_2 = 0.0408$	$wR_2=0.0711$	$wR_2=0.1880$	
<i>R</i> indices	$R_1 = 0.0297$	$R_1 = 0.1285$	$R_1 = 0.0173$	$R_1 = 0.0270$	$R_1 = 0.0828$	
(all data)	$wR_2 = 0.0750$	$wR_2 = 0.2894$	$wR_2 = 0.0412$	$wR_2 = 0.0719$	$wR_2 = 0.1955$	
CCDC number	1948366	1948365	1948370	1948368	1948367	
$R_{1} = \Sigma Fo - Fc / \Sigma Fo , wR_{2} = \left[\Sigma [w(Fo^{2} - Fc^{2})^{2}] / \Sigma w(Fo^{2})^{2} \right]^{1/2}$						

Table S2 Crystallographic data of complexes 1a-1c, 2a and 2b

Complex	2d	2d-Me	2e-Me
Formula	C ₃₈ H ₅₂ AuN ₃ O	C40H56AuN3O	C44H60AuN3O
Formula weight	763.79	791.84	843.91
Temperature	100 K	100 K	100 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Cl_2/c_1	$P2_1/n$	$P2_1/c$
a (Å)	11.2640(16)	13.025(2)	16.597(3)
b (Å)	23.609(3)	17.695(3)	14.750(2)
c (Å)	13.2861(19)	17.750(3)	18.101(3)
α (deg)	90	90	90
β (deg)	99.420(2)	99.930(3)	100.144(3)
γ (deg)	90	90	90
Volume (Å ³)	3485.6(9)	4029.7(12)	4362.1(12)
Ζ	4	4	4
F (000)	1552	1616.0	1728.0
θ (deg) for collection	3.58 to 21.36	2.58 to 30.08	2.29 to 27.30
Index range	-15<=h<=15	-16<=h<=16	-20<=h<=20
	-31<=k<=31	-21<=k<=21	-18<=k<=18
	-17<=1<=17	-21<=l<=21	-22<=l<=22
Reflections collected	38486	74742	81069
Unique (<i>R</i> _{int})	133 (0.0613)	9925 (0.0367)	9898 (0.0651)
data/restrain/parameter	4332/368/290	7902/0/420	8570/0/455
Goodness of Fit	1.065	1.041	1.008
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0322$	$R_1 = 0.0189$	$R_1 = 0.0229$
	$wR_2 = 0.0778$	$wR_2 = 0.0457$	$wR_2 = 0.0483$
<i>R</i> indices (all data)	$R_1 = 0.0387$	$R_1 = 0.0259$	$R_1 = 0.0354$
	$wR_2=0.0811$	$wR_2=0.0478$	$wR_2=0.0511$
CCDC number	1948369	1948371	1948372
$R_1 = \Sigma Fo - Fc / \Sigma Fo , wR_2 =$	$= \left[\Sigma \left[w (Fo^2 - Fc^2)^2 \right] / \Sigma w (Fo^2 - Fc^2)^2 \right] $	$(Fo^2)^2]^{1/2}$	

 Table S3 Crystallographic data of complexes 2d, 2d-Me and 2e-Me

Electrochemistry

All the CV and DPV measurements are carried out in anhydrous aerated CH₃CN solution at room temperature with tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF) using as supporting electrolyte. Due to the close lying oxidation potentials of this series of complexes with the widely used reference ferrocene, decamethyl ferrocene with cathodically shifted oxidation potential is employed to avoid the overlap of the oxidation peaks of the sample and the reference. To determine the relative redox potential of decamethyl ferrocene compared to ferrocene, CV and DPV scans are performed first with these two references only as shown in Figure S2. Both two references present reversible oxidation peaks as shown in CV plots. According to the DPV results, when the redox potentials of ferrocene are fixed to 0.0 V, those of decamethyl ferrocene are found between -0.54 and -0.55 V. Thus, by setting the decamethyl ferrocene reference.



CV plot (left) and DPV (right) curves of ferrocene (Fc) and decamethyl ferrocene (DMFc) are recorded in MeCN at RT under inert atmosphere with TBAPF as supporting electrolyte





Measurements are carried out in MeCN at RT under inert atmosphere. TBAPF is used as supporting electrolyte and decamethyl ferrocene is used as internal reference. The average of the oxidation and reduction peak values of ferrocene is set to 0 V



Measurements are carried out in MeCN at RT under inert atmosphere versus ferrocene. TBAPF is used as supporting electrolyte and decamethyl ferrocene is used as internal reference. Potentials are reported by setting ferrocene at 0 V.



Measurements are carried out in MeCN at RT under inert atmosphere. TBAPF is used as supporting electrolyte and decamethyl ferrocene is used as internal reference. The average of the oxidation and reduction peak values of ferrocene is set to 0 V



Theoretical calculations

Geometry optimizatized ground state and lowest triplet states from DFT calculations at B3LPY/LACVP* level in the gas phase.



B3LYP/LACVP* level

Table S4 Natural transition orbital (NTO) analysis of (carbene)Au(aryl) complexes

All the calculations are carried out using TD-DFT method at CAM-B3LYP/LACVP* level in gas phase based on the optimized ground state geometry. All H atoms are omitted for clarity, diagrams are shown with holes in green and particles in yellow. All the information for ICT states are printed in blue.



20	A ICT/LC 3.15 eV (97.7%)	ICT 3.51 eV (99.1%)	MLCT 3.90 eV (99.2%)	LC/MLCT 4.36eV (99.5%)
2e	ICT	ICT	MLCT	LC/MLCT
	3.04 eV (97.4%)	3.40 eV (99.1%)	3.89 eV (99.2%)	4.36 eV (99.5%)
2d-Me				- And
	$\operatorname{ICT}_{2,06,0\mathbf{V}}(07,09/1)$	$\frac{\text{ICT}}{2.30 \text{ eV}(00.09/)}$	MLCT	LC/MLCT
2e-Me				
	2.96 eV (97.7%)	3.29 eV (99.1%)	3.86 eV (99.2%)	4.30 eV (99.7%)
(DAC)AuC	MLCT	MLCT		
-	3.17 eV (96.7%)	3.49 eV (98.2)		
(MAC)AuCl	MLCT	MLCT		
	3.74 eV (99.5%)	4.15 eV (99.5%)		

	State	Energy (eV/nm)	Osc.	Major Contribution
	S ₃ (LC/MLCT)	3.94/315	0.001	HOMO-5→LUMO (67%) HOMO-7→LUMO (12%) HOMO-15→LUMO (6%) HOMO-2→LUMO (5%)
1 a	S_2 (ICT)	3.75/331	0.284	HOMO→LUMO (94%)
	S_1 (MLCT)	3.19/389	0.005	HOMO-2→LUMO (89%)
	T ₁ (MLCT)	3.05/407	0.000	HOMO-2→LUMO (80%) HOMO-5→LUMO (8%) HOMO-7→LUMO (6%)
	S ₃ (LC/MLCT)	4.01/309	0.001	HOMO-8→LUMO (61%) HOMO-11→LUMO (16%)
16	S ₂ (ICT)	3.42/363	0.226	HOMO→LUMO (88%) HOMO-2→LUMO (9%)
10	S ₁ (MLCT)	3.29/377	0.006	HOMO-3→LUMO (86%)
	T ₁ (MLCT)	3.12/397	0.000	HOMO-3→LUMO (69%) HOMO-8→LUMO (9%) HOMO-11→LUMO (10%)
	S ₃ (LC/MLCT)	3.98/312	0.001	HOMO-9→LUMO (64%) HOMO-11→LUMO (15%) HOMO-19→LUMO (6%)
1c	S ₂ (MLCT)	3.23/384	0.004	HOMO-1→LUMO (25%) HOMO-3→LUMO (64%)
	S_1 (ICT)	2.95/420	0.278	HOMO→LUMO (94%)
	T ₁ (ICT)	2.73/454	0.000	HOMO→LUMO (82%) HOMO-2→LUMO (8%)
	S ₃ (ICT)	4.45/279	0.290	HOMO→LUMO (90%)
20	S ₂ (LC/MLCT)	4.36/284	0.002	HOMO-4→LUMO (46%) HOMO-6→LUMO (6%) HOMO-7→LUMO (6%) HOMO-13→LUMO (20%)
2a	S ₁ (MLCT)	3.94/315	0.009	HOMO-1→LUMO (86%)
	T ₁ (MLCT)	3.72/333	0.000	HOMO-1 \rightarrow LUMO (50%) HOMO-4 \rightarrow LUMO (23%) HOMO-6 \rightarrow LUMO (6%) HOMO-7 \rightarrow LUMO (7%)
	S ₃ (LC/MLCT)	4.40/282	0.003	HOMO-3→LUMO (5%) HOMO-7→LUMO (38%) HOMO-9→LUMO (8%) HOMO-11→LUMO (9%) HOMO-17→LUMO (19%)
2b	S ₂ (ICT)	4.20/295	0.355	HOMO→LUMO (78%) HOMO-2→LUMO (13%)
	S ₁ (MLCT)	4.02/308	0.009	HOMO-3→LUMO (84%)
	T ₁ (³ Cz)	3.56/348	0.000	HOMO→LUMO+8 (12%) HOMO-1→LUMO+3 (67%) HOMO-10→LUMO+15 (6%)

Table S5 Calculated transition properties of the T₁ and S₁-S₃ states.

			HOMO-8 \rightarrow LUMO (42%)	
	S ₃ (LC/MLCT)	4.39/283	0.002	HOMO-10 \rightarrow LUMO (7%) HOMO-11 \rightarrow LUMO (8%)
				HOMO-17 \rightarrow LUMO (20%)
	S ₂ (MLCT)	3.98/312	0.008	HOMO-1→LUMO (82%)
20	S ₁ (ICT)	3.75/331	0.365	HOMO→LUMO (87%)
		3,35/370	0.000	HOMO→LUMO+8 (13%)
	T_1 (ICT)			HOMO \rightarrow LUMO+5 (6%)
	-1()			HOMO \rightarrow LUMO (47%)
				$\frac{\text{HOMO-2} \rightarrow \text{LUMO}(6\%)}{\text{HOMO-4} \rightarrow \text{LUMO}(47\%)}$
				HOMO- $7 \rightarrow I \text{ LUMO} (5\%)$
	S_3 (LC/MLCT)	4.36/284	0.002	HOMO-8 \rightarrow LUMO (6%)
		1.50/201	0.002	HOMO-13 \rightarrow LUMO (15%)
2d				HOMO-14→LUMO (5%)
	S ₂ (MLCT)	3.90/318	0.008	HOMO-1→LUMO (87%)
	S_1 (ICT)	3.51/353	0.316	HOMO→LUMO (94%)
	T_1 (ICT)	3.15/394	0.000	HOMO→LUMO (78%)
	11(101)			$HOMO \rightarrow LUMO + 11 (5\%)$
		1 22/207	0.002	HOMO-5 \rightarrow LUMO (56%)
	S_3 (LC/MLCT)	4.32/287	0.002	HOMO-13 \rightarrow LUMO (10%)
2d-Me	S ₂ (MLCT)	3.88/319		$\frac{11000-14}{1100}$
20-1110			0.008	HOMO-5 \rightarrow LUMO (5%)
	S ₁ (ICT)	3.39/366	0.299	HOMO→LUMO (93%)
	T_1 (ICT)	3.06/405	0.000	HOMO→LUMO (80%)
	T ₁ (ICT)	3.06/405	0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%)
	T ₁ (ICT)	3.06/405	0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%)
	T ₁ (ICT) S ₃ (LC/MLCT)	<u>3.06/405</u> 4.36/284	0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%)
	T ₁ (ICT) S ₃ (LC/MLCT)	<u>3.06/405</u> 4.36/284	0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%)
2e	T ₁ (ICT) S ₃ (LC/MLCT)	<u>3.06/405</u> 4.36/284	0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%)
2e	T ₁ (ICT) S ₃ (LC/MLCT)	3.06/405 4.36/284 3.89/319	0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%)
2e	T ₁ (ICT) S ₃ (LC/MLCT) S ₂ (MLCT) S ₁ (ICT)	3.06/405 4.36/284 3.89/319 3.40/365	0.000 0.002 0.008 0.306	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%)
2e	$\frac{T_1 (ICT)}{S_3 (LC/MLCT)}$ $\frac{S_2 (MLCT)}{S_1 (ICT)}$	3.06/405 4.36/284 3.89/319 3.40/365 2.04/408	0.000 0.002 0.008 0.306	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%)
2e	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$	3.06/405 4.36/284 <u>3.89/319</u> 3.40/365 3.04/408	0.000 0.002 0.008 0.306 0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (76%) HOMO→LUMO+10 (5%)
2e	$\frac{T_1 (ICT)}{S_3 (LC/MLCT)}$ $\frac{S_2 (MLCT)}{S_1 (ICT)}$ $T_1 (ICT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408	0.000 0.002 0.008 0.306 0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (76%) HOMO→LUMO+10 (5%)
2e	$\frac{T_1 (ICT)}{S_3 (LC/MLCT)}$ $\frac{S_2 (MLCT)}{S_1 (ICT)}$ $T_1 (ICT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408	0.000 0.002 0.008 0.306 0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (76%) HOMO→LUMO (7%)
2e	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288	0.000 0.002 0.008 0.306 0.000 0.000	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (76%) HOMO→LUMO+10 (5%) HOMO-3→LUMO (7%) HOMO-3→LUMO (7%) HOMO-5→LUMO (49%)
2e	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288	0.000 0.002 0.008 0.306 0.000 0.001	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%) HOMO-2→LUMO (5%) HOMO-3→LUMO (7%) HOMO-3→LUMO (7%) HOMO-13→LUMO (7%) HOMO-15→LUMO (7%)
2e	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288	0.000 0.002 0.008 0.306 0.000 0.001	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (76%) HOMO→LUMO+10 (5%) HOMO-3→LUMO (7%) HOMO-3→LUMO (7%) HOMO-13→LUMO (7%) HOMO-15→LUMO (7%) HOMO-15→LUMO (15%)
2e 2e-Me	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$ $S_{3} (ICT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288 4.30/288	0.000 0.002 0.008 0.306 0.000 0.000 0.001 3.99×10 ⁻⁵	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%) HOMO-2→LUMO (5%) HOMO-3→LUMO (76%) HOMO-3→LUMO (7%) HOMO-13→LUMO (7%) HOMO-13→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (15%) HOMO-15→LUMO (15%)
2e 2e-Me	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$ $S_{3} (ICT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288 4.30/288	0.000 0.002 0.008 0.306 0.000 0.001 3.99×10 ⁻⁵	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%) HOMO-2→LUMO (5%) HOMO-3→LUMO (7%) HOMO-3→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (7%) HOMO-15→LUMO (7%) HOMO-15→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (83%) HOMO-1→LUMO (83%)
2e 2e-Me	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$ $S_{3} (ICT)$ $S_{2} (MLCT)$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288 4.30/288 3.87/320	0.000 0.002 0.008 0.306 0.000 0.000 3.99×10 ⁻⁵ 0.011	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%) HOMO→LUMO (76%) HOMO-3→LUMO (5%) HOMO-3→LUMO (76%) HOMO-3→LUMO (7%) HOMO-13→LUMO (7%) HOMO-13→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (83%) HOMO-1→LUMO (83%) HOMO-1→LUMO (85%)
2e 2e-Me	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $T_{1} (ICT)$ $S_{4} (LC/MLCT)$ $\frac{S_{3} (ICT)}{S_{2} (MLCT)}$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288 4.30/288 3.87/320 3.29/377	0.000 0.002 0.008 0.306 0.000 0.000 3.99×10 ⁻⁵ 0.011 0.283	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO-2→LUMO (5%) HOMO-2→LUMO (5%) HOMO-3→LUMO (7%) HOMO-13→LUMO (7%) HOMO-13→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (83%) HOMO-1→LUMO (83%) HOMO-1→LUMO (85%) HOMO-2→LUMO (6%) HOMO-1→LUMO (94%)
2e 2e-Me	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $\frac{S_{4} (LC/MLCT)}{S_{3} (ICT)}$ $\frac{S_{2} (MLCT)}{S_{2} (MLCT)}$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288 4.30/288 3.87/320 3.29/377 2.96/419	$\begin{array}{c} 0.000\\ 0.002\\ 0.008\\ 0.306\\ 0.000\\ \hline \\ 0.000\\ \hline \\ 3.99 \times 10^{-5}\\ \hline \\ 0.011\\ 0.283\\ \hline \\ 0.000\\ \hline \end{array}$	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-8→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%) HOMO→LUMO (76%) HOMO-3→LUMO (7%) HOMO-3→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (15%) HOMO-15→LUMO (83%) HOMO-1→LUMO (83%) HOMO-5→LUMO (6%) HOMO-5→LUMO (94%) HOMO-5→LUMO (94%)
2e 2e-Me (DAC)AuCl	$\frac{T_{1} (ICT)}{S_{3} (LC/MLCT)}$ $\frac{S_{2} (MLCT)}{S_{1} (ICT)}$ $\frac{S_{4} (LC/MLCT)}{S_{3} (ICT)}$ $\frac{S_{2} (MLCT)}{S_{2} (MLCT)}$ $\frac{S_{1} (ICT)}{T_{1} (ICT)}$ $\frac{S_{2} (XM-LCT)}{S_{2} (XM-LCT)}$	3.06/405 4.36/284 3.89/319 3.40/365 3.04/408 4.31/288 4.30/288 3.87/320 3.29/377 2.96/419 3.82/324	0.000 0.002 0.008 0.306 0.000 0.000 3.99×10 ⁻⁵ 0.011 0.283 0.000 5.00×10 ⁻⁶	HOMO→LUMO (80%) HOMO-4→LUMO (39%) HOMO-5→LUMO (11%) HOMO-7→LUMO (5%) HOMO-13→LUMO (9%) HOMO-15→LUMO (11%) HOMO-2→LUMO (87%) HOMO→LUMO (94%) HOMO→LUMO (76%) HOMO→LUMO (76%) HOMO-2→LUMO (5%) HOMO-3→LUMO (76%) HOMO-4LUMO (76%) HOMO-110 (5%) HOMO-3→LUMO (7%) HOMO-13→LUMO (7%) HOMO-15→LUMO (15%) HOMO-15→LUMO (15%) HOMO-15→LUMO (83%) HOMO-1→LUMO (83%) HOMO→LUMO (79%) HOMO→LUMO (79%) HOMO→LUMO (79%) HOMO→LUMO (79%) HOMO→LUMO (79%)

				HOMO-3→LUMO (8%)
				HOMO-7→LUMO (9%)
				HOMO-2→LUMO (65%)
	T_1 (MLCT)	3.17/391	0.000	HOMO-3→LUMO (7%)
				HOMO-7→LUMO (20%)
				HOMO→LUMO (66%)
	S_2 (XM-LCT)	4.57/271	0.001	HOMO-2→LUMO (7%)
				HOMO-3→LUMO (7%)
	S ₁ (MLCT)	4.15/299		HOMO→LUMO (10%)
			0.007	HOMO-2→LUMO (24%)
				HOMO-3→LUMO (40%)
(MAC)AUCI				HOMO-7→LUMO (13%)
			0.000	HOMO→LUMO (6%)
				HOMO-2→LUMO (18%)
	T_1 (MLCT)	3.74/332		HOMO-3→LUMO (31%)
				HOMO-7→LUMO (25%)
				HOMO-11→LUMO (5%)

Complex	S0 dipole μ (μ _z)	S1 dipole μ (μ _z)	T1 dipole μ (μ _z)
1a	4.7 (4.7)	8.5 (-8.5)	6.5 (-6.5)
1b	7.7 (7.7)	4.9 (-4.8)	7.4 (-7.4)
1c	5.7 (5.7)	30.5 (-30.5)	19.9 (-19.9)
2a	7.5 (6.8)	5.0 (3.8)	6.2 (-5.0)
2b	10.5 (9.9)	3.4 (-0.7)	10.2 (9.7)
2c	8.6 (8.0)	23.1 (-22.8)	3.7 (1.7)
2d	5.5 (5.4)	24.1 (-23.7)	11.6 (-11.0)
2d-Me	5.8 (4.8)	23.2 (-22.7)	12.3 (-11.7)
2e	5.8 (4.8)	24.6 (-24.2)	10.3 (-9.6)
2e-Me	6.3 (5.4)	23.3 (-22.8)	10.8 (-10.1)

Dipole moments are obtained from TD-DFT calculations where μ_z is the projection of μ along the Au-C_{aryl} bond axis. Negative values indicate dipole moments are opposite in direction from that of the ground state. All dipole moments values are presented in Debye.

In order to assess the effect of solvation on the photophysics of the systems under study, TDDFT calculations were performed using the IEF-PCM solvation model for meTHF at the CAM-B3LYP/LACVP* level in the non-equilibrium limit through the ptLR-ptSS approach implemented in Q-Chem. The ptSS-ptLR approach has been shown to accurately predict solvatochromic shifts¹. The results of the solvation calculations are presented in the table below. It can be seen that relative to the gas phase

calculations, the non-equilibrium solvation results indicate a significant hypsochromic shift for the MLCT and ICT transitions consistent with the absorption spectra for these compounds which show a hypsochromic shift with increasing polarity. It should be noted that in all cases when the solvation model is included, the S_1 state still maintains the same character, while the triplet states show reordering in a few cases due to the proximity of multiple CT and LE states which are affected to different degrees by solvation effect as seen the table below

	CAM-B3LYP/LACVP*				CAM-B3LYP/LACVP*(IEF- PCM:ptSS/ptLR:meTHF)			
		S ₁		T ₁	S ₁		T ₁	
1a	3.19	MLCT	3.05	MLCT	3.39	MLCT	3.23	MLCT
1b	3.29	MLCT	3.12	MLCT	3.45	MLCT	3.12	LC(Cz)
1c	2.95	ICT	2.73	ICT	3.03	ICT	2.88	ICT
2a	3.94	MLCT	3.72	MLCT	4.20	MLCT	3.45	LC(Ph)
2b	4.02	MLCT	3.56	LC(Cz)	4.23	MLCT	3.09	LC(Cz)
2c	3.75	ICT	3.35	LC(TPA)	3.91	ICT	3.11	LC(TPA)
2d	3.51	ICT	3.15	ICT	3.62	ICT	3.19	ICT
2d-Me	3.39	ICT	3.06	ICT	3.55	ICT	3.14	ICT
2e	3.40	ICT	3.04	ICT	3.50	ICT	3.03	ICT
2e-Me	3.29	ICT	2.96	ICT	3.44	ICT	3.00	ICT

Table 57 Calculated excited state properties in vacuum and in survent

The S_1 geometries were optimized at the CAM-B3LYP/LACVP* level and the results are included in the table below. Consistent with the experimental spectra, large stokes shifts are predicted in all cases.

	S ₀ optimized geometry	S ₁ optimized geometry
1a	3.19	2.71
1b	3.29	2.75
1c	2.95	2.18
2a	3.94	3.17
2b	4.02	3.25
2c	3.75	3.16
2d	3.51	2.69
2d-Me	3.39	2.56
2e	3.40	2.51
2e-Me	3.29	2.39

Table S8 Calculated S_1 energies in S_0 and S_0 optimized geometries.

Steady-state photophysical characterization

The emission properties of **1a** and **2a** in fluid solution are investigated in MeCy. No data at 77 K are available because of poor solubility. Complexes **1b** and **2b** were investigated in MeTHF due to their poor solubility in MeCy at both room temperature and 77 K.

|--|

Complex	Absorption peaks/nm (Molar extinction coefficient/×10 ³ L/(mol×cm))						
Complex	THF	Cyclohexane					
1a	261 (9.0), 352 (5.2), 407 (1.0)	262 (11.5), 375 (8.2), 417 (1.7)					
16	263 (25.4), 294 (16.6), 331 (5.5), 345 (5.8),	262 (28.0), 294 (20.6), 331 (7.3), 345 (7.3),					
10	388 (4.2)	418 (5.4)					
1c	300 (19.9), 455 (4.6)	304 (22.9), 495 (7.2)					
2a	288 (5.6), 335 (1.0)	230 (29.5), 308 (11.1), 344 (2.7)					
26	238 (53.7), 260 (30.2), 294 (19.7), 319 (8.6),	238 (47.7), 262 (26.7), 294 (16.5), 334 (8.4),					
20	328 (8.6), 343 (7.0)	344 (8.5)					
2c	299 (20.2), 354 (9.3)	292 (17.6), 382 (7.3)					
2d	237 (16.5), 252 (16.0), 365 (4.8)	245 (21.2), 387 (7.0)					
2e	256 (19.2), 386 (6.6)	247 (17.2), 415 (5.8)					
2d-Me	254 (14.8), 382 (6.1)	254 (12.0), 410 (5.6)					
2d-Me	402 (5.8)	252 (11.2), 435 (5.7)					

Commlan	Room temperature				77 K		
Complex	λ_{em} (nm)	Φ_{PL}	τ (ns)	$k_{\rm r} (10^5 {\rm s}^{-1})$	$k_{\rm nr} (10^5 { m s}^{-1})$	$\lambda_{em} (nm)$	τ (μs)
				MeTHF			
1a ^a	_	-	_	_	_	_	-
1b	586	< 0.001	1.3[c]	<7.7	>7600	505	44.4
2 a ^a	_	-	—	-	—	-	-
2b	366	< 0.001	9.2	<1.1	>1080	410,438,463	second
MeCy							
1a	508	< 0.001	4.9	<2.0	>2000	–[b]	-[b]
1 b ^b	_	-	—	_	_	-	-
2a	466	< 0.001	4.9	<2.0	>2000	–[b]	-[b]
2 b ^b	_	_	_	_	_	_	-
1 wt% doped PS film							
1a	486	< 0.001	3.6[c]	<2.8	>2700	470,485,512	44.6
1b	526	< 0.001	10.7[c]	<1.0	>900	530	43.5
2a	458	< 0.001	3.0[c]	<3.3	>3330	430,456	82.6
2b	389	< 0.001	5.2	<1.9	>1900	410,440,463	second
[a] No spectral available due to strong emission from the BHT stabilizer: [b] no spectral data due to noor							

Table S10. Luminescent properties of complex 1a, 1b, 2a and 2b

[a] No spectral available due to strong emission from the BHT stabilizer; [b] no spectral data due to poor solubility in MeCy; [c] Calculated from the weighted average of the two contributions to τ .

Figure S10. Emission spectra of complexes 1a, 1b, 2a and 2b

The emission bands of **1a** and **2a** at 77 K in PS film display spectral peaks due to Raman scattering. Owing to the low-lying LUMO energy of **1b** with DAC than **2b** with MAC, the ³MLCT state that is the lowest triplet excited state in **1b** becomes higher than carbazolyl based ³LC state. Consequently, the emission of **1b** at 77 K in PS film is kept as broad and featureless MLCT emission, but that of **2b** presents distinguishing ³LC emission exclusively from the carbazolyl moiety with a lifetime on the second scale. Although the k_r values of these four complexes at room temperature are found to be on the order of 10⁵ s⁻¹, the k_{nr} values are roughly of three orders of magnitude larger leading to the poor luminescence efficiency. Strickler-Berg analysis, which has been proven successful for organic fluorophores, takes extinction spectral data to estimate oscillator strength for the transition between ground state and the first singlet excited state. Then, radiative decay rate for emission can be predicted in turn. The analysis requires the following data: absorption maximum in wavenumbers, integrated area of the S_0 - S_1 transition in wavenumbers and the extinction coefficient in L/(mol×cm). Here, the integrated area is estimated by integrating half of the low energy ICT absorption band and double it numerically aiming to avoiding the overlap with the high-energy ligand-based absorption. The equation used is shown below:

$$k_{fl} = 2.88 \times 10^{-9} \vartheta_0^2 \int \varepsilon d\vartheta$$

Where k_{fl} is the predicted radiative decay rate, ϑ_0 is the wavenumber of the absorption maximum, ε is the molar extinction coefficient.

2d/2d-Me and 2e/2e-Me in cyclohexane

Figure S14. Emission spectra of complexes 2d/2d-Me and 2e/2e-Me at RT and at 77 K in solution

(a) in MeCy (b) in MeTHF. Negative solvatochromism behavior is also observed in these complexes. This behavior can be explained by the large molecular dipole moment of the ground state and the oppositely directed dipole moment of the excited state, which follows the same principle as in complexes **1c**.

1H NMR analysis

The signal of the ortho-methyl groups is marked by circles (filled in complexes and empty in free ligands)

Figure S16. Variable temperature ¹H NMR spectra of 2e-Me from -70 °C to RT in acetone-d₆.

VT-NMR was carried out on complex **2e-Me**, and the proton resonance of the ortho-methyl groups on the aryl ligand do not broaden or split down to -70 °C, indicating that the rotation around Au–C_{aryl} bond, while hindered, is not blocked compared to analogs without these substituents.

Temperature-dependent transient photophysical characterizations

Complex	two-level model				
Complex	ΔE_{ST} (cm ⁻¹)	$\tau_{\rm fl} \left(ns \right)$	$ au_{ m ph}~(\mu s)$		
1c	680	15	53		
2c	1100	6.7	40		
2d	900	13	44		
2d-Me	1100	12	55		
2e	940	14	62		
2e-Me	940	18	70		

Table S11 Photophysical data derived from two-level Boltzmann fits to temperaturedependent lifetimes

The contribution of TADF and direct phosphorescence can be estimated using the fluorescence/phosphorescence rates and ΔE_{ST} data. The corresponding equations are given below:

$$\% \text{TADF} = \left[1 - \left(1 + \frac{k_{fl}}{3k_{ph}} e^{-\frac{\Delta E_{ST}}{k_B T}} \right)^{-1} \right] \times 100$$

% Phosphorescence =
$$\left[\left(1 + \frac{k_{fl}}{3k_{ph}} e^{-\frac{\Delta E_{ST}}{k_B T}} \right)^{-1} \right] \times 100$$

Figure S20 ¹**H NMR spectra of the intermediate organic compounds and boronic species in CDCl3 (DMSO for 4-dimethylamino-2,6-dimethl phenyl boronic acid)** All the spectra were recorded using a 400 MHz spectrometer.

Figure S21 ¹**H NMR spectra of the (carbene)Au(aryl) complexes in** *d*⁶**-acetone** All the spectra were recorded using a 400 MHz spectrometer.

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Figure S22 ¹³C NMR spectra of the (carbene)Au(aryl) complexes in d^6 -acetone All the spectra were recorded using a 400 MHz spectrometer.

1. Mewes, J. M.; You, Z. Q.; Wormit, M.; Kriesche, T.; Herbert, J. M.; Dreuw, A., Experimental Benchmark Data and Systematic Evaluation of Two a Posteriori, Polarizable-Continuum Corrections for Vertical Excitation Energies in Solution. *Journal of Physical Chemistry A* **2015**, *119* (21), 5446-5464.