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Thermally Robust and Tunable Phosphorescent Gold(III) Complexes Bearing (N^N)-Type Bidentates as Ancillary Chelates

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Abstract[.] Phosphorescent monocyclometalated gold(III) complexes and their possible applications in organic light emitting diodes (OLED's) can be significantly enhanced with their improved thermal stability by suppressing the reductive elimination of the respective ancillary ligands. A rational tuning of the π -conjugation of the cyclometalating ligand in conjunction non-conjugated 5,5'-(1-methylethyl-idene)-bis(3with the trifluoromethyl)-1H-pyrazole were used as a strategy to achieve room temperature phosphorescence emission in a new series of gold(III) complexes. Photophysical studies of the newly synthesised characterised and complexes revealed phosphorescent emission of the complexes at room temperature in solution, thin films when doped in poly(methyl methacrylate) (PMMA) as well as in 2-Me-THF at 77 K. The complexes exhibit highly tunable emission behaviour with photoluminescent quantum efficiencies up to 22% and excited state lifetimes in the range of 63-300 µs. Detailed photophysical investigations in combination with DFT and TD-DFT calculations corroborate that the emission properties are strongly dictated by both the cyclometalating ligand and the ancillary chelating ligand. Thermogravimetric studies further show that the thermal stability of the Au(III) complexes has been drastically enhanced, making these complexes further attractive for OLED applications.

Introduction

During the last two decades, organotransition-metal based triplet emitters have gained an incredibly high interest due to their great potential towards light emitting applications.^[1] In particular, triplet based emitters can be used for the fabrication of highly efficient phosphorescent organic light emitting diodes (PhOLEDs). Compared to the already extensively investigated triplet based emitters containing Pt(II)^[1a, 2] and Ir(III)^[1b, 1c, 3] as metal centres, the research on Au(III)^[4] is rather less explored. The introduction of gold(III) as metal centre has attracted high attention in the past

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vears and shows great potential towards full-color display technologies and energy-saving solid-state lighting.^[5] Despite the fact that gold as a "heavy-metal" exhibits a very high spinorbit coupling (SOC) constant ξ for its 5d electrons (5100 cm⁻¹), thermally accessible and low-lying metal-centred (MC) d-d levels are known to quench the luminescent states through an energy transfer or thermal equilibration, which leads to non-radiative deactivation of the excited states.^[6] However, it has been found that the introduction of strong field ligands can increase the lowlying dd levels of the Au(III) centre.[6a] Also, the high positive redox potential E°(Au³⁺/Au) of 1.50 V makes Au(III) complexes susceptible to undergo reduction leading to decomposition. Such reductions have been suppressed through the utilization of a tridentate ligand scaffold leading to bis-cyclometalated complexes of the type $[Au(C^N^{A}C)L]^{[7]}$ and $[Au(N^{A}C^{A}C)L]^{[8]}$ where L = aryl, alkyne were showed to be suitable for achieving room temperature emission. Although stability and luminescence was achieved using the tridentate systems, these complexes displayed emission only in the blue-green, green and red part of the electromagnetic spectrum. We recently demonstrated that blue emission could be achieved by using deep monocyclometalated Au(III) complexes with aryls or alkynes as ancillary ligands.^[9] One of the drawbacks of these systems is the lack of stability in comparison to the bis-cyclometalated systems due to the possibility of reductive eliminations. We considered that this reduced stability could be overcome by utilizing bidentate ancillary chelates. However, a previous work reported on a monocyclometalated bis-bidentate complex of the type $[Au(C^N)(C^C)]$ where $(C^N) = 2$ -phenylpyridine (2-ppy) and (C^{C}) = biphenyl proved to be unstable.^[10] In this context, we sought to investigate new luminescent organogold(III) complexes with dianionic chelates as ancillary ligands where the possibility for reductive eliminations is suppressed. We hypothesized that the dianionic (N^N) bidentates such as 5,5'bis(trifluoromethyl)-2H,2H'-3,3'-bispyrazolate (bipz) and 5,5'-(1methylethylidene)-bis(3-trifluoromethyl-1H-pyrazolate) (mepz) were considered as ideal ancillary ligand candidates to achieve highly stable and emissive monocyclometalated gold(III) complexes. Such ligands have been previously employed and has been limited to platinum(II) and iridium(III) complexes.^[2f, 11] The cyclometalating ligands L1 through L5 were chosen to demonstrate the high tunability of the photophysical properties across the visible part of the electromagnetic spectrum. Ligands a and b were chosen as an alternative dianionic chelate to the currently existing monodentate aryl and alkyne ligands in order to further improve the photophysical properties and increase the thermal stability of the complexes. To the best of our knowledge organogold(III) complexes of the type [Au(C^N)(N^N)] are unknown. Herein, we report the synthesis, characterisation and excited-state properties of a series of a new class of charge neutral gold(III) complexes based on the [Au(C^N)(N^N)] structural motif.

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Results and Discussion

Synthesis and characterisation

The target complexes 1a-6b were synthesised in 15-85% yield starting from the corresponding gold(III)-dichloride precursors I-VI and the successive ligation of the (N^N)-type ligands $bipzH_2$ (**a**) or mepzH₂ (**b**) according to the synthetic strategy shown in Scheme 1. Precursors were synthesised by slightly modified literature procedures.^[2f, 9a, 12] The final complexes were characterised by ¹H, ¹³C and ¹⁹F NMR; HR-ESI-MS and elemental analysis. The ¹H NMR signals for the α proton of the pyridyl unit revealed to appear in a narrow range of 10.18-10.36 ppm for the complexes 1a, 1b, 2a, 2b, 3b and 5b. For complexes bearing a para substituted NMe₂group on the pyridine ring (4b, 6b), the signals for the corresponding α protons of the pyridyl unit appeared at 9.37– 9.65 ppm. This significant upfield shift ($\delta\Delta$) of ~0.70 ppm can be explained due to the strong π -donating effect of the NMe₂group. The ¹H NMR signals for the pyrazolic CH protons on the bipz and mepz framework were found to be at 6.97 ppm (1a, 2a) and 6.47-6.68 ppm (1b, 2b, 3b, 4b, 5b, 6b). Additionally, ¹⁹F NMR studies of all complexes revealed two singlets from -59.0 to -61.8 ppm for the chemically inequivalent CF₃-groups on the pyrazolic rings.

Crystal structure determination

In order to obtain further insight into the structural conformation around the Au(III) centre, single crystals were obtained and subjected to an X-ray diffraction analysis. Suitable crystals of complexes **2b**, **3b**, **4b** and **5b** were obtained via vapor diffusion of pentane to a concentrated solution of CH_2Cl_2 and slow evaporation at 3–4 °C. The crystal structures of the complexes are shown in Figure 1 with the selected bond distances and bond angles summarized in Table 1. Crystallographic details for the complexes **2b**, **3b**, **4b** and **5b** are provided in the Supporting Information. The solid-state structures revealed an slightly distorted square planar structure around the Au(III) centre. The Au–C_{Ar} and the Au–

 N_{Py} bond lengths do not vary significantly and were found in the range between 2.012(5)–2.036(3) Å and 2.015(4)– 2.047(2) Å. These observations show that the bond lengths are only slightly influenced by the electronic nature of the different monocyclometalated ligands. However, Au–N_{mepz} bond lengths *trans* to the coordinated monocyclometalated aryls (2.061(5)–2.087(2) Å) were found to be significantly longer than the Au–N_{mepz} bond lengths which are *cis* bound (1.993(2)–2.007(2) Å). The bond length differences of 0.094(3) Å (**2b**), 0.068(3) Å (**3b**), 0.66(6) Å (**4b**) and 0.061(4) Å (**5b**) between the Au–N_{mepz} bonds can be ascribed to the *trans* influence exerted by the ligand.

Table 1. Selected bond distances [Å] and angles [°] for complexes 2b, 3b,

4b and 5b.				
Bond	2b	3b	4b	5b
Au–C _{Ar}	2.025(3)	2.033(3)	2.012(5)	2.036(3)
Au–N _{py}	2.029(2)	2.035(2)	2.015(4)	2.047(2)
Au–N _{mepz} (cis)	2.087(2)	2.075(2)	2.061(5)	2.061(3)
Au–N _{mepz} (<i>trans</i>)	1.993(2)	2.007(2)	1.995(4)	2.000(2)
C _{Ar} -Au-N _{py}	80.82(10)	81.28(10)	80.90(2)	81.28(11)
N _{mepz} -Au-N _{mepz}	84.18(10)	84.20(9)	84.24(18)	84.01(11)
N _{py} -Au-N _{mepz} (<i>cis</i>)	98.33(9)	97.14(9)	98.26(18)	95.68(11)
N _{py} –Au–N _{mepz} (<i>trans</i>)	176.42(10)	176.20(9)	176.95(19)	177.48(10)
C _{Ar} –Au–N _{mepz} (<i>cis</i>)	170.88(11)	176.77(10)	177.40(2)	176.32(11)
C _{Ar} –Au–N _{mepz} (<i>trans</i>)	96.30(10)	97.21(10)	96.50(2)	98.94(11)



Figure 1. Molecular structures of 2b (top left), 3b (top right), 4b (bottom left) and 5b (bottom right) with displacement ellipsoids drawn at the 30% probability level. Selected hydrogen atoms are omitted for clarity for complexes 4b and 5b.

Photophysical properties

The electronic absorption spectra for complexes 1a-1b and 2a-2b, measured in CH₂Cl₂ are shown in Figure 2. The UV-Vis profiles for the complexes that possess the same monocyclometalated framework do not vary significantly. The spectra of complexes 1a and 1b display two distinct transitions at around 230 nm and a lower energy transition at around 320 nm, while 2a and 2b have a distinct transition peak at lower energy between 380-390 nm. The calculated absorption spectra of 1a-1b and 2a-2b obtained from TD-DFT calculations on the DFT optimized ground state structures (see Figure S32 and Computational Details) reproduce very well the experimental data with lowest energy bands around 300 nm for compounds 1a-1b and around 370 nm for compounds 2a-2b. The analysis of the lowest singlet excited states and the frontier molecular orbitals (FMO's) revealed that in the case of 2a and 2b the corresponding absorption can be exclusively assigned to a ligand-centred (LC) $\pi_{(C^{n}N)}$ \rightarrow $\pi^{*}_{(C^{n}N)}$ transition originating from a HOMO \rightarrow LUMO electronic excitation, while in the case of 1a and 1b the low-energy band can be assigned to a mixture of ligandto-ligand (LL) $\pi_{(N^{n}N)} \rightarrow \pi^{*}_{(C^{n}N)}$ and LC $\pi_{(C^{n}N)} \rightarrow \pi^{*}_{(C^{n}N)}$ transitions mainly from HOMO-1 \rightarrow LUMO excitations. This strongly suggests that the ancillary ligands $bipzH_2$ (a) and mepzH₂ (b) have no significant influence on the lowest singlet excited states.





The emission properties of these compounds were investigated at room temperature and at 77 K in different media (Table 2). The normalized emission spectra of 1b, 2a and 2b recorded in 2-Me-THF at 77 K are depicted in Figure 3. Interestingly, compound 1a is non-emissive in solution at room temperature and at 77 K, compounds 1b and 2a only exhibit emission at 77 K, while compound 2b is emissive at room temperature in solution, in solid state and when doped into PMMA. It seems that in order to render the complexes with the (N^N) ancillary ligands emissive at room temperature, it is imperative that the lowest energy charge transfer (CT) is only localised on a highly *π*-conjugated monocyclometalated ligand. Two strategies were followed in a step-wise manner to alter the CT. One of the strategy involved the destabilization of the HOMO of the (N^N) ancillary ligand in order to prevent its involvement in the CT. This was achieved by separating the π -conjugation in bipzH₂ (a) through an incorporation of a methylene bridge. This strategy was applied to obtain complex 1b, which displayed an emission with distinctive peaks at 458 nm, 492 nm (λ_{max}) and 520 nm albeit only at 77 K. The success of the second hypothesis targeting to increase the π -conjugation of the monocyclometalated ligand was achieved by synthesising complex 2a, which unlike 1a displayed emission at 77 K with λ_{max} values at 526 nm and 570 nm. Compared to compound 1b, a bathochromic shift of about 90 nm was observed. This shift can be explained by the larger π -conjugation resulting in a lower energy LC $\pi_{(C^{n}N)}$ $\rightarrow \pi^*_{(C^{\Lambda}N)}$ transition, which is responsible for the emission. The emission profile of 2b at 77 K in 2-Me-THF is very similar to 2a with no significant energy differences but as already mentioned 2b was found to be emissive at room temperature in solution, in solid state and doped in PMMA. The successive changes made both to the monocyclometalated moiety (i.e. extended π -conjugation) as well on the ancillary ligand (interrupted π -conjugation) revealed to be the key elements to achieve improved emission properties based on these type of monocyclometalated Au(III) complexes.

The successful structural and electronic changes that lead to achieve emission at room temperature were applied further for the synthesis of four additional Au(III) complexes (3b-6b) bearing varyingly conjugated monocyclometalated scaffold and mepzH₂ (**b**) as the ancillary ligand. The UV-Vis spectra measured in CH₂Cl₂ are depicted in Figure 4. The significant differences in the absorption profiles are suggestive that the electronic properties are mainly influenced by the cyclometalated ligand. The lowest energy absorption peak of complex 3b exhibits a hypsochromic shift of about 20 nm compared to compound 2b. The substitution of an NMe2group on the para position of the pyridine ring of complex 4b resulted in a hypsochromic shift of the lowest energy peak. This is due to the π -donating effect of the NMe₂ group that destabilizes the LUMO of the complex.[9a] Overall, the following trend is observed for the absorption maxima for the complexes 6b > 3b ~ 4b > 2b > 5b.

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Figure 3. Normalized emission spectra of complexes 1b, 2a and 2b in 2-Me-THF at 77 K.



Complementary TD-DFT calculations carried out on **3b–6b** gave the same trend (Table S2, Figure S33) and allowed to assign the lowest energy absorption bands to LC $\pi_{(C^{\Lambda}N)} \rightarrow \pi^*_{(C^{\Lambda}N)}$ transitions for **3b**, **4b** and **6b**. The broad profile of the UV-Vis spectrum of **5b** between 330 and 430 nm is also correctly reproduced by the calculations which additionally show that the low-energy bands arise from an admixture of ¹LL $\pi_{(C^{\Lambda}N)} \rightarrow \pi^*_{(N^{\Lambda}N)}$ and ¹LC $\pi_{(C^{\Lambda}N)} \rightarrow \pi^*_{(C^{\Lambda}N)}$ singlet excited states. It is important to note that the metal centre is present in the FMO's involved in the electronic excitations but its participation is rather small.

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As expected, similar to **2b** all new complexes **3b–6b** are emissive at room temperature in solution, in solid state and doped in PMMA. Emission properties measured in degassed CH_2CI_2 at room temperature as well as doped in PMMA are shown in Figure 6.

Emission measurements in thin films were carried out on small glass plates, which were spin-coated from a solution containing 3 wt% of emitter (dopant) in PMMA (host). The emission maxima shifts follow a similar trend **6b** > **3b** > **4b** > **2b** >> **5b** as observed in the case of the UV-Vis spectra for the complexes. This trend is in good agreement with the extended π -system of the cyclometalating ligand and the corresponding increase of the HOMO-LUMO gap and supports the fact that the emission is caused by a ${}^{3}LC \pi_{(C^{N}N)} \rightarrow \pi^{*}_{(C^{N}N)}$ centred triplet excited state. Both assumptions are confirmed by the calculations since the calculated lowest triplet excited states T₁ originate from HOMO \rightarrow LUMO excitations for all **2b–6b** compounds, where the FMO's are almost exclusively localised on the cyclometalating ligands and the metal centre (Figure 5), and that the calculated S₀ –

T1 energies and HOMO – LUMO gaps follow the experimental trend (6b = 2.89 / 4.79 eV, 3b = 2.59 / 4.27, 4b = 2.53 / 4.30, 2b = 2.40 / 4.02, and 5b = 2.18 / 3.94), respectively (Tables S2-S3). In general, the emission spectra measured at room temperature exhibit a much broader and less resolved profile compared to the spectra obtained at 77 K. This is due to the less distinct vibronic substates resulting in the decreased intensity of the distinctive peaks. The emission maxima appear between 487 nm (6b) and 678 nm (5b) and have an average Stokes-shift of about 150-250 nm. Concentration dependent emission studies of all the complexes in CH₂Cl₂ (c $\approx 10^{-6} - 10^{-4}$ M) revealed no shift in the λ_{max} or development of an additional low energy band supporting the absence of any aurophilic interactions in solution and precluding excimeric metal to metal charge transfer (³MMLCT) transitions. For all emission experiments, which were performed at room temperature, the coordinates of the complexes are plotted on a CIE 1931 color space chromaticity diagram to show the perceived emission color of the luminescent complexes (Figure 6).



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Figure 6. Normalized emission spectra in degassed CH₂Cl₂ of complexes 2b-6b (top left) and in PMMA films (bottom left) of complexes 2b-5b at 298 K, CIE-1931 diagrams of 2b-6 in degassed CH₂Cl₂ (top right) and 2b–5b wt% PMMA right). of in 3 in (bottom

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	Absorption (CH ₂ Cl ₂)		Emission			
Complex	λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)	Medium (T/K)	λ_{max} /nm $(\tau_0/\mu s)^{[d]}$	$\phi_{em} \left(\%\right)^{[e]}$	k _r [×10 ³ s⁻¹]	k _{nr} [×10 ³ s ⁻¹]
1a	231 (30533) 319 (5781)	2-Me-THF (77) PMMA (298) CH ₂ Cl ₂	[a]	[a]		Ţ
1b	230 (25087) 318 (7076)	2-Me-THF (77) PMMA (298) CH ₂ Cl ₂	458, 492, 520 [b] [b]	_ (b)		
2a	230 (28454) 388 (16067)	2-Me-THF (77) PMMA (298) CH ₂ Cl ₂ (298)	526, 570 խ	— [b]		
2b	229 (25071) 268 (18868) 295 (16460) 385 (17414)	2-Me-THF (77) PMMA (298) CH ₂ Cl ₂ (298)	518 (642.27), 559 (638.30) 536 (333.16), 573 (280.44) 541 (19.35), 580 (35.56)	- 20.88 7.23	0.63 3.74	2.37 47.95
3b	228 (42443) 298 (13529) 362 (17532)	PMMA (298) CH ₂ Cl ₂ (298)	492 (248.90), 526 (184.19) 497 (0.06), 534	21.87 3.47	0.88 579.95	3.14 1613.36
4b	228 (36267) 284 (27507) 342 (28125) 360 (25120)	PMMA (298) CH ₂ Cl ₂ (298)	518 (252.57), 552 (299.10) 514 (101.02), 552 (53.92)	19.48 6.85	0.77 0.68	3.19 9.22
5b	229 (39426) 279 (12084) 300 (13346) 358 (10304)	PMMA (298) CH ₂ Cl ₂ (298)	576 (41.58), 621 (32.39) 578 (25.16), 625 (20.39)	13.80 0.77	3.32 0.31	20.73 39.44
6b	229 (37425) 279 (45250) 323 (17802)	PMMA (298) CH ₂ Cl ₂ (298)	ା 487 (94.71), 520 (60.16)	^[c]	0.08	10.48

[a] no emission. [b] no emission at 298 K. [c] very week emission. [d] averaged lifetime. [e] absolute quantum yields.

Thermogravimetric analysis (TGA)

The thermal stability was investigated for selected complexes **1a**, **1b**, **2a**, **3b** and **5b** using TGA. The onset of degradation (T_d) for the samples are provided in the Supporting Information (Table S1 and Figures S2–S6) and show similar temperature ranges between 340–365 °C for the complexes bearing 2-ppy as the ligand. Compared to already investigated monocyclometalated gold(III) complexes bearing two perfluorinated aryls as ancillary ligands, ^[9a, 10] the studied compounds exhibit a significantly increased thermal stability by about 70 – 100 °C.

Electrochemical properties

Cyclic voltammetry (CV) studies were carried out for all final complexes **1a–6b** in DMF at room temperature and displayed irreversible reduction peaks in the range from -1.51 to -1.90 V (vs. Fc^{0/+} couple). No oxidation peaks were observed (see Figures S7–S14). The reduction peaks are similar to previously reported monocyclometalated complexes and are ascribed to be a predominately cyclometalating ligand centred electrochemical event.^[10, 12c] Electrochemical data for all final complexes **1a–6b** are represented in Table 3.

Table 3. Electrochemical reduction potentials (E_{pc}) for all final complexes.^[a]

'		
	Complex	E _{pc} [V]
	1a	-1.51
	1b	-1.53
	2a	-1.59
	2b	-1.61
	3b	-1.52
	4b	-1.90
	5b	-1.27, -1.78
	6b	-1.80

[a] CV performed in DMF with 0.1 M [nBu₄N][PF₆] as supporting electrolyte and a glassy-carbon electrode against $Fc^{0^{+}}$ as reference at a scan rate of 100 mVs⁻¹ at 25 °C.

Conclusions

A new series of luminescent monocyclometalated Au(III) complexes bearing 5,5'-bis(trifluoromethyl)-2H,2'H-3,3'bipyrazole (bipzH₂, a) and 5,5'-(1-methylethyl-idene)-bis(3trifluoromethyl-1H-pyrazole (mepzH₂, **b**) as ancillary bidentates have been synthesised and characterised. A judicious combination of various cyclometalating ligands with extended π-system and the ancillary N^N chelate with a nonconjugated variant was strategically chosen to tune the triplet excited state systematically to achieve room temperature emission from the new series of complexes. DFT and TD-DFT calculations lend further support to the successful tuning of the triplet excited state. Photophysical investigations performed for all the final complexes showed a tunable emission behavior across the visible spectrum in thin films and solution at room temperature with photoluminescent quantum efficiencies as high as 21%. TGA studies confirmed the pronounced thermal stability of the complexes. An increase of decomposition temperatures of over 70°C-100°C in comparison to the corresponding monocyclometalated diaryl complexes and dialkyne complexes, respectively were achieved. The new complexes with their significantly improved thermal stability and luminescence efficiencies open avenues for employing these materials in applications in OLED devices and other relevant light emitting applications.

Experimental Section

General procedure

Unless otherwise stated, all manipulations were carried out without special precautions for excluding air and moisture. $^1\text{H},~^{13}\text{C}$ and ^{19}F NMR were recorded on either Bruker AV-500, AV-400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (δ 0.00 ppm) using the residual protio solvent peaks as internal standards (¹H NMR experiments) or the characteristic resonances of the solvent nuclei (13C NMR experiments). Fluorine (¹⁹F NMR experiments) spectra were referenced to CFCI₃ (δ 0.00 ppm). Coupling constants (J) are quoted in Hertz (Hz), and the following abbreviations are used to describe the signal multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet). Elemental microanalysis was carried out with Leco CHNS-932 analyzer. TLC analysis was performed on precoated Merck Silica Gel 60F254 slides and visualized by luminescence quenching either at 254 nm or 365 nm. Column chromatographic purification (length 20.0 cm; diameter 2.0 cm) of the synthesised products was performed with silica gel 60, 230-400 mesh. UV-Vis measurements were carried out on a PerkinElmer Lambda 19 UV-Vis spectrophotometer. Emission spectra were acquired on an Edinburgh FLS980 spectrophotometer using 450W Xenon lamp excitation by exciting at the longest wavelength absorption maxima. All samples for emission spectra were degassed by 15 min N_2 flow. 77 K emission spectra were measured in frozen 2-methyltetrahydrofuran (2-Me-THF) glass. Absolute quantum yields were measured using and integrating sphere from Edinburgh Instrument. YAG:Ce (powder) was used as a calibration reference with Φ_{em} = 97%. Thin films were spin coated on glass plates (8 x 8 mm) from a solution of poly(methyl methacrylate) PMMA and the corresponding Au(III) complexes in CH₂Cl₂ at 298 K (estimated uncertainty \pm 15%). Phosphorescence lifetimes in PMMA films were measured with an Edinburgh instruments laser flash photolysis spectrophotometer LP920 or a microsecond flash lamp μ F2 from Edinburgh instruments. For the excitation source, a Nd:YAG laser (371 nm) equipped with a single monochromator was acquired. Excitation range for the μF2 lamp is 230-1000nm. Photoexcited emission color CIE-1931 chromaticity diagrams were determined from

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normalized emission spectra and the ColorCalculator from Osram Sylvania. Cyclic voltammetry experiments were measured with a Methrom 757 VA Computrace using a glassy carbon electrode (d = 2 mm) with a Pt counter electrode vs. Ag/AgCl reference electrode. Starting materials were purchased from commercial suppliers and used without further purification.

Synthesis and characterisation

General Procedure for the Synthesis of (1a–6b): To a suspension of 3 eq. (with respect to the Au(III)-precursor) NaOAc in 1,4-dioxane, 1 eq. of the gold(III)-dichloride and 1 eq. of the corresponding bipyrazoles were added slowly. The reaction mixtures were heated to 110 °C and stirred for 24h. After the reactions were completed, the mixtures were quenched with H_2O and the final products were extracted with CH_2Cl_2 . The combined organic layers were dried over MgSO₄. Filtration and removal of the solvent *in vacuo* delivered the crude products, which were purified by column chromatography.

[Au(ppy)(bipz)] (1a): A colorless solid was observed. Eluent: EtOAc/hexane 1:1. Yield 83%. ¹H NMR (400 MHz, DMSO-d₆, 278 K): δ (ppm) 10.33 (d, 1H, ³J_{HH} = 6.2, py.), 8.99 (d, 1H, ³J_{HH} = 7.1, arom.), 8.43 (q, 2H, ³J_{HH} = 7.3, arom.), 7.99 (dd, 1H, ³J_{HH} = 7.3, ⁴J_{HH} = 1.7, arom.), 7.89 (td, 1H, ³J_{HH} = 6.4, ⁴J_{HH} = 2.1, arom.), 7.48 (td, 2H, ³J_{HH} = 4.5, ⁴J_{HH} = 2.0, arom.), 6.97 (s, 1H, bipz), 6.96 (s, 1H, bipz). ¹³C NMR (125 MHz, DMSO-d₆, 278 K): δ (ppm) 164.1, 149.3, 144.7, 144.5, 144.0, 143.5, 143.3, 141.5 (q, CF₃), 141.3 (q, CF₃), 131.1, 129.9, 129.2, 126.0, 125.0, 122.5 (q, CCF₃), 122.0 (q, CCF₃), 121.8, 99.6, 99.2. ¹⁹F NMR (188 MHz, DMSO-d₆, 278 K): δ (ppm) –59.2 (s, CF₃), – 59.7 (s, CF₃). Elemental analysis calcd (%) for C₁₉H₁₀AuF₆N₅: C, 36.85; H, 1.63; N, 11.31. Found: C, 36.72; H, 1.66; N, 11.33%. (+)-HR-ESI-MS (MeOH): calcd for C₁₉H₁₁AuF₆N₅⁺ [M + H]⁺: m/z 620.0579.

[Au(ppy)(mepz)] (1b): A colorless solid was obtained. Eluent: EtOAc/hexane 1:1. Yield: 25%. ¹H NMR (400 MHz, CD₂Cl₂, 278 K): *δ* (ppm) 10.36 (dd, 1H, ³J_{HH} = 6.1, ⁴J_{HH} = 1.5, py.), 8.15–8.21 (m, 2H, arom.), 8.01 (dd, 1H, ³J_{HH} = 8.1, ⁴J_{HH} = 1.5, arom.), 7.69 (dd, 1H, ³J_{HH} = 7.6, ⁴J_{HH} = 1.7, arom.), 7.57 (dd, 1H, ³J_{HH} = 7.5, ⁴J_{HH} = 1.5, arom.), 7.44 (dd, 2H, ³J_{HH} = 7.9, ⁴J_{HH} = 1.5, arom.), 6.51 (s, 1H, mepz), 6.47 (s, 1H, mepz), 1.86 (s, 6H, CH₃). ¹³C NMR (125 MHz, CD₂Cl₂, 278 K): *δ* (ppm) 166.4, 154.1, 154.0, 151.6, 148.0, 143.8, 143.6 (q, CF₃), 143.6, 133.8, 132.2, 129.9, 125.4, 124.7, 123.4 (q, CCF₃), 122.9 (q, CCF₃), 121.5, 99.9, 99.8, 35.6, 30.0. ¹⁹F NMR (188 MHz, CD₂Cl₂, 278 K): *δ* (ppm) –61.0 (s, CF₃), –61.5 (s, CF₃). Elemental analysis calcd (%) for C₂₂H₁₆AuF₆N₅: C, 39.95; H, 2.44; N, 10.59. Found: C, 39.81; H, 2.36; N, 10.54%. (+)-HR-ESI-MS (MeOH): calcd for C₂₂H₁₇AuF₆N₅⁺ [M + H]⁺: m/z 662.1049. Found: 662.1052.

[Au(dmfpy)(bipz)] (2a): A pale yellow solid was observed. Eluent: EtOAc/hexane 1:1. Yield: 63%. ¹H NMR (400 MHz, DMSO-d₆, 278 K): δ (ppm) 10.29 (dd, 2H, ³*J*_{HH} = 5.4, ⁴*J*_{HH} = 0.7, py.), 9.56 (d, 1H, ⁴*J*_{HH} = 0.7, arom.), 8.38–8.49 (m, 2H, arom.), 8.28 (s, 1H, arom.), 7.82–7.86 (m, 1H, arom.), 7.65–7.69 (m, 2H, arom.), 7.43–7.52 (m, 2H, arom.), 6.98 (s, 1H, bipz), 6.96 (s, 1H, bipz), 1.55 (s, 6H, CH₃). ¹³C NMR (125 MHz, DMSO-d₆, 278 K): δ (ppm) 164.3, 154.3, 153.8, 149.1, 144.7,

144.0, 143.6, 143.5, 141.5, 141.4 (q), 141.1 (q), 140.8, 137.6, 128.7, 127.6, 124.2, 123.2, 122.5, 122.2, 121.6, 121.3, 120.6, 119.9, 99.5, 99.2, 46.7, 26.6. ¹⁹F NMR (188 MHz, DMSO-d_6, 278 K): δ (ppm) – 59.2 (s, CF₃), -60.1 (s, CF₃). Elemental analysis calcd (%) for C₂₈H₁₈AuF₆N₅: C, 45.73; H, 2.47; N, 9.52. Found: C, 45.58; H, 2.40; N 9.41%. (+)-HR-ESI-MS (MeOH): calcd for C₂₈H₁₉AuF₆N₅⁺ [M + H]⁺: m/z 736.1205. Found: 736.1203.

[Au(dmfpy)(mepz) (2b): A colorless solid was observed. Eluent: EtOAc/hexane 1:1. Yield: 51%. ¹H NMR (400 MHz, CD₂Cl₂, 278 K): *δ* (ppm) 10.32 (m, 1H, py.), 8.71 (s, 1H, arom.), 8.18 (dd, 1H, ³J_{HH} = 8.1, ⁴J_{HH} = 1.5, arom.), 8.06 (dd, 1H, ³J_{HH} = 8.1, ⁴J_{HH} = 1.4, arom.), 7.71–7.73 (m, 2H, arom.), 7.38–7.54 (m, 4H, arom.), 6.54 (s, 1H, mepz), 6.53 (s, 1H, mepz), 1.89 (s, 6H, CH₃), 1.26 (m, 3H, CH₃), 0.88 (m, 3H, CH₃). ¹³C NMR (125 MHz, CD₂Cl₂, 278 K): *δ* (ppm) 166.6, 162.2, 155.0, 154.0, 151.4, 147.5, 143.6, 143.3 141.5, 138.6, 135.0, 129.3, 128.2, 125.6, 124.0, 123.3, 121.4, 121.2, 119.6, 110.6, 102.7, 102.5, 99.9, 99.8, 47.6, 35.6, 32.2, 27.3, 23.2, 14.5. ¹⁹F NMR (188 MHz, CD₂Cl₂, 278 K): *δ* (ppm) –61.0 (s, CF₃), –61.4 (s, CF₃). Elemental analysis calcd (%) for C₃₁H₂₄AuF₆N₅: C, 47.89; H, 3.11; N, 9.01. Found: C, 50.47; H, 4.11; N, 7.77%. (+)-HR-ESI-MS (MeOH): calcd for C₃₁H₂₅AuF₆N₅⁺ [M + H]⁺: m/z 778.1674. Found: 778.1672.

[Au(dbfpy)(mepz)] (3b): A colorless solid was observed. Eluent: EtOAc/hexane 1:2. Yield: 15%. ¹H NMR (400 MHz, DMSO-d₆, 278 K): δ (ppm) 10.18 (dd, 1H, ³*J*_{HH} = 6.0, ⁴*J*_{HH} = 1.0, py.), 8.95 (dd, 1H, ³*J*_{HH} = 8.1, ⁴*J*_{HH} = 1.1, arom.), 8.59 (td, 1H, ³*J*_{HH} = 7.9, ⁴*J*_{HH} = 1.4, arom.), 8.28 (d, 1H, ³*J*_{HH} = 8.4, arom.), 8.24 (d, 1H, ³*J*_{HH} = 7.6, arom.), 8.07 (d, 1H, ³*J*_{HH} = 8.4, arom.), 7.93–7.89 (m, 2H, arom.), 7.66 (td, 1H, ³*J*_{HH} = 7.8, ⁴*J*_{HH} = 1.2, arom.), 7.92–7.89 (m, 2H, arom.), 7.66 (td, 1H, ³*J*_{HH} = 7.8, ⁴*J*_{HH} = 1.2, arom.), 7.52 (t, 1H, ³*J*_{HH} = 7.5, arom.), 6.68 (s, 1H, mepz), 6.67 (s, 1H, mepz), 1.86 (s, 6H, CH₃). ¹³C NMR (125 MHz, DMSO-d₆, 278 K): δ (ppm) 162.5, 155.9, 153.5, 153.4, 150.5, 149.9, 144.7, 144.5, 141.9 (q, CCF3), 141.5 (q, CCF3), 128.7, 127.7, 126.2, 124.4, 124.2, 124.2, 124.1, 122.7 (q, CF₃), 122.4, 122.3 (q, CF₃), 122.3, 121.6, 112.0, 99.6, 99.5, 34.6. ¹⁹F NMR (188 MHz, DMSO-d₆, 278 K): δ (ppm) –59.1 (s, CF₃), –59.6 (s, CF₃). Elemental analysis calcd.(%) for C₂₈H₁₈AuF₆N₅O: C, 44.75; H, 2.41; N, 9.32. Found: C, 44.65; H, 2.33; N, 9.22%. (+)-HR-ESI-MS (MeOH): calcd for C₂₈H₁₉AuF₆N₅O⁺ [M + H]⁺: m/z 752.1154. Found: 752.1150.

[Au(dmfapy)(mepz)] (4b): A colorless solid was observed. Eluent: EtOAc/hexane 1:1. Yield: 65%. ¹H NMR (500 MHz, CD₂Cl₂, 278 K): *δ* (ppm) 9.65 (d, 1H, ³J_{HH} = 7.3, py.), 8.69 (s, 1H, arom.), 7.71–7.69 (m, 1H, arom.), 7.67 (s, 1H, arom.), 7.48–7.47 (m, 1H, arom.), 7.38 (dd, 2H, ³J_{HH} = 5.5, ⁴J_{HH} = 3.1, arom.), 7.05–7.04 (m, 1H, arom.), 6.60–6.58 (m, 1H, arom.), 6.50 (s, 1H, mepz), 6.49 (s, 1H, mepz), 3.27 (s, 6H, CH₃), 1.89 (s, 6H, CH₃). ¹³C NMR (125 MHz, CD₂Cl₂, 278 K): *δ* (ppm) 164.5, 157.0, 154.7, 154.3, 154.1, 148.9, 146.2, 142.5, 142.2, 138.9, 129.5, 128.8, 128.0, 125.0, 123.2, 121.3, 105.5, 101.8, 99.6, 99.4, 47.5, 40.4, 35.6, 27.4. ¹⁹F NMR (188 MHz, CD₂Cl₂, 278 K): *δ* (ppm) –60.9 (s, CF₃), –61.3 (s, CF₃). Elemental analysis calcd (%) for C₃₃H₂₉AuF₆N₆: C, 48.30; H, 3.56; N, 10.24. Found: C, 48.47; H, 3.91; N, 9.27%. (+)-HR-ESI-MS (MeOH): calcd for C₃₃H₃₀AuF₆N₆⁺ [M + H]⁺: m/z 821.2096. Found: 821.2095.

[Au(btph)(mepz)] (5b): A yellow solid was observed. Eluent: EtOAc/CH₂Cl₂/hexane 1:2:2. Yield: 56%. ¹H NMR (500 MHz, CD₂Cl₂, 278 K): δ (ppm) 10.35 (dd, 1H, ³J_{HH} = 6.1, ⁴J_{HH} = 1.4, py.), 8.16 (dd, 1H, ³J_{HH} = 7.8, ⁴J_{HH} = 1.5, arom.), 7.89 (d, 1H, ³J_{HH} = 8.4, arom.), 7.74 (d, 1H, ³J_{HH} = 7.1, arom.), 7.48 (ddd, 1H, ³J_{HH} = 7.6, ³J_{HH} = 6.1, ⁴J_{HH} = 1.5, arom.), 7.42 (ddd, 1H, ³J_{HH} = 8.2, ³J_{HH} = 7.1, ⁴J_{HH} = 1.2, arom.), 7.22 (ddd, 1H, ³J_{HH} = 8.3, ³J_{HH} = 7.1, ⁴J_{HH} = 1.1, arom.), 6.96 (d, 1H, ³J_{HH} = 8.1, arom.), 6.56 (s, 1H, mepz), 6.54 (s, 1H, mepz), 1.96 (s, 6H, CH₃). ¹³C NMR (125 MHz, CD₂Cl₂, 278 K): δ (ppm) 161.7, 154.2, 153.1, 151.1, 147.6, 144.2, 140.5, 139.3, 129.5, 128.7, 128.0, 127.5, 125.5, 123.3, 122.8, 121.7, 100.3, 100.2, 35.9. ¹⁹F NMR (188 MHz, CD₂Cl₂, 278 K): δ (ppm) –61.2 (s, CF₃), –61.8 (s, CF₃). Elemental

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analysis calcd (%) for $C_{21}H_{16}AuF_6N_5S$: C, 40.18; H, 2.25; N, 9.76. Found: C, 41.51; H, 2.32; N, 8.37%.

[Au(dbfapy)(mepz)] (6b): A colorless solid was observed. Eluent: EtOAc/CH₂Cl₂ 1:1. Yield: 19%. ¹H NMR (400 MHz, DMSO-d₆, 278 K): δ (ppm) 9.37 (d, 1H, ³J_{HH} = 7.4, py.), 8.97 (s, 1H, arom.), 8.46 (s, 1H, arom.), 8.19 (d, 1H, ³J_{HH} = 7.9, arom.), 7.80 (d, 1H, ³J_{HH} = 8.1, arom.), 7.60 (t, 1H, ³J_{HH} = 7.9, arom.), 7.53–7.48 (m, 2H, arom.), 6.88 (d, 1H, ³J_{HH} = 8.0, arom.), 6.68 (s, 1H, mepz), 6.63 (s, 1H, mepz), 1.84 (s, 6H, CH₃). ¹³C NMR (125 MHz, CDCl₃, 278 K): δ (ppm) 163.6, 156.9, 156.4, 155.7, 154.0, 152.4, 148.0, 144.5, 139.7, 127.6, 127.0, 124.6, 124.3, 122.9, 121.7, 112.5, 111.4, 105.0, 102.3, 100.0, 35.3. ¹⁹F NMR (188 MHz, CD₂Cl₂, 278 K): δ (ppm) –59.0 (s, CF₃), –59.3 (s, CF₃). (+)-HR-ESI-MS (MeOH): calcd for C₃₀H₂₄AuF₆N₆O⁺ [M + H]^{*}: m/z 795.1576. Found: 795.1575.

Computational details

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were used to investigate the luminescent properties of the selected compounds 1a-2a and 1b-6b. The calculations were performed with the Gaussian 09 program package^[13] using the hybrid functional PBE1PBE^[14] associated with the Stuttgart/Dresden effective core potentials (SDD) basis set^[15] for the Au centre augmented with one *f*-polarization function ($\alpha = 1.050$), with the standard 6-31+G(d) basis set^[16] for the remaining atoms, and with the conductive polarizable continuum model (CPCM)^[17] to take the solvent effects into account (dichloromethane). The DFT-optimized ground state structures were obtained by restricted calculations while the lowest triplet state structures were obtained by unrestricted DFT calculations, all calculations were carried out without symmetry restriction for the molecules. The final geometries were confirmed to be potential energy minima by vibrational frequency calculations at the same level of theory (no imaginary - negative frequency). On the DFT-optimized ground state S_0 geometries, TD-DFT calculations^[18] were used to produce the first 25 lowest singlet-singlet and the first 3 singlet-triplet vertical excitations with the corresponding energies. transition coefficients and oscillator strengths. The frontier orbital surfaces and spin density distributions reported in the manuscript and Supporting Information were generated by GaussView^[19] on Gaussian 09^[13] formatted checkpoint output files with isovalues set to 0.02 and 0.004, respectively.

X-ray crystallography

Single-crystal X-ray diffraction data were collected for complexes 2b, 3b, 4b and 5b at 183(1) K on Rigaku Oxford Diffraction diffractometers using a single wavelength X-ray source (Mo ${\rm K}_{\alpha}$ radiation: λ = 0.71073 Å): XtaLAB Synergy, Dualflex, Pilatus 200K diffractometer^[20] associated to an Oxford liquid-nitrogen Cryostream cooler for 3b and 5b, Xcalibur/Ruby area-detector diffractometer^[20] associated to an Oxford Instruments Cryojet XL cooler for 4b, and SuperNova/Atlas area-detector diffractometer^[20] associated to an Oxford Instruments Cryojet XL cooler for 2b. The selected single crystals were mounted using polybutene oil on a flexible loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption correction^[21] were performed with the program suite CrysAlis^{Pro. [22]} Using Olex2, ^[23] the structures were solved with the SHELXT^[24] small molecule structure solution program and refined with SHELXL2014/7^[25] by full-matrix least-squares minimization on F^2 . $\mathsf{PLATON}^{[26]}$ was used to check the result of the X-ray analyses. For more details about the data collection and refinement parameters, see the CIF files. CCDC 1559440 (2b), 1559441 (5b), 1559442 (3b) and

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1559441 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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FULL PAPER

Room temperature emission from monocyclometalated Au(III) dianionic complexes bearing chelate with also (N^N)-type significantly improved thermal stability has been successfully achieved by tuning the triplet excited state through the judicious combination of both the cyclometalating ligand and the ancillary ligand dianionic (N^N) chelate.



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Thermally Robust and TunablePhosphorescentGold(III)Complexes Bearing (N^N)-TypeBidentates as Ancillary Chelates