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Deep-blue thermally activated delayed fluorescence of a CF3-substituted carbene-metal-amide complex†

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A gold-based carbene-metal-amides (CMA) complex, BICAuBGCF3, with a 2-(trifluoromethyl)benzoguanidine amide (L) ligand was prepared in good yields and characterized. The CF3-substituted amide donor ligand resulted in a 0.27 eV stabilization of the highest occupied molecular orbital (HOMO) and a wide energy gap of 2.97 eV. In fluid media, the complex experiences dynamic behavior between two isomeric forms, which reduces the blue luminescence quantum yield to 43%. In the solid state, the complex shows bright deep-blue thermally activated delayed fluorescence at 432 nm with 60% luminescence quantum yield owing to a small singlet triplet energy gap (ΔE_{ST}) down to 54 meV. Radiative rates (k_r) were calculated to be up to $1.4 \times 10^6 \text{ s}^{-1}$ in amorphous polystyrene media, demonstrating the BICAuBGCF3 complex as a promising material for optoelectronic applications.

Introduction

Bright and stable thermally activated delayed fluorescence (TADF) luminophores are highly sought after by the academic community and industry for optoelectronic applications, particularly as organic light-emitting diodes (OLEDs), photovoltaics and sensors. 1-3 This is because of their ability to harvest singlet and triplet excitons via reverse intersystem crossing (rISC) from the triplet (T_1) state to the singlet state (S_1) .⁴⁻⁹ Among the most high-performance TADF materials, carbene-metal-amide (CMA) materials have emerged as a promising class of organometallic TADF materials owing to their facile synthesis and spectacular performance in OLED devices. 10-12 Their common molecular design is based on a d¹⁰-coinage metal (Cu, Ag or Au) with a near-linear arrangement of a π -donor amide and a π -acceptor carbene ligand in trans-position to each other. Various CMA materials have demonstrated luminescence across the whole visible spectrum with submicrosecond emission lifetimes and near unity photoluminescence quantum yields (PLQYs). 13-16

Several orientations are possible because of the conformational flexibility of the donor and acceptor ligands of CMAs: fully-twisted, co-planar, tilted and twisted/tilted CMAs. Romanov et al. demonstrated that twisted and tilted geometry can achieve the highest radiative rates among CMAs with a similar molecular design.¹⁷ Such conformational flexibility between carbene and amide moieties enables the control of the frontier orbital overlap integral (SHO) between the highest occupied molecular orbital (HOMO), located on the amide donor ligand, and the lowest unoccupied molecular orbital (LUMO), located over the M-carbene bond. High-performance CMA materials possess charge transfer (CT) characteristics for the first singlet (S_1) and triplet (T_1) excited states. Recent studies have highlighted the importance of the molecular design principle minimising the frontier orbital overlap integral to reduce the energy difference between 1 CT and 3 CT excited states (ΔE_{ST}) and accelerate the radiative rates to above 10⁶ s⁻¹. 18,19

Recent works on CMA materials have highlighted the role of the energy difference between locally excited triplet (3LE) and CT emissive states in CMA materials $(\Delta E_{\text{(CT-3LE)}})^{20}$, where increasing the energy of the 3LE state relative to the manifold of CT states enables near unity photoluminescence quantum yields (PLQYs) and high radiative rates of TADF. 21 CMA compounds are known for their high ground and excited state dipole moments, where emission energies are sensitive to their molecular environment; for example, this has allowed the "tuning" of electroluminescence from green to sky-blue using a suitable host media. 18b,20 Efficient blue emission from CMA complexes can be achieved by attaching electron-withdrawing

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Scheme 1 Molecular structures of blue light-emitting CMA complexes.

CF₃ groups to the amide moiety to stabilize the HOMO energy and widen the energy gap (Scheme 1). This strategy achieved deep blue emission TADF for mono-CF3-substituted CMA complexes; however, di-CF3 substituted CMA complexes resulted in long-lived phosphorescent emission from the locally excited state of the carbazolide ligand, 3LE(Cz). 20-22 Such CF3-substituted CMA complexes appeared highly suitable for the fabrication of the energy transfer OLEDs.²³

Recently, it was found that the energy of the ³LE state can be increased for aza-CMA materials (Scheme 1), enabling faster and more efficient deep-blue TADF emission.²⁴ Electronwithdrawing aza-nitrogen substitution in para-position to the amide-N atom24 have been further extended towards BG-CMA materials (Scheme 1).25 The use of the benzoguanidine (BG) ligand with multiple aza-N atom substitutions in the donor ligand enabled the formation of champion BG-CMA materials exhibiting deep-blue TADF luminescence with high radiative rates of up to $4.69 \times 10^6 \text{ s}^{-1}$ due to a $\Delta E_{\text{(CT-3LE)}}$ of up to -0.5 eVand a reduced HOMO/LUMO overlap integral $(S_{H/L} = 0.25)$.²⁵ This outstanding photophysical behaviour motivated the team to build on the synergy between the two molecular design strategies for deep-blue CMA materials (Scheme 1). Herein, we investigated the first example of a CMA material containing an electron-withdrawing CF3 moiety in a BG-donor ligand to demonstrate deep-blue TADF and reveal the structure-property relationship.

Results and discussion

A carbene-metal-amide (CMA) complex, BICAuBGCF3, was prepared by reacting the halide complex BiCAACAuCl with

2-(trifluoromethyl)-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (BGCF3) in the presence of the KO^tBu base in THF following our previously published protocol in high yield. The complex was found to be stable in air for several months. 25 This gold-based complex was characterized using 1H, 19F and ¹³C{¹H} NMR spectroscopy (ESI†) and high-resolution mass spectrometry (HRMS). The product demonstrated high solubility in aromatic solvents (toluene, chlorobenzene, and 1,2difluorobenzene), THF, and dichloromethane but was only sparingly soluble in hexane. On first inspection, the ¹H NMR spectrum of BICAuBGCF3 appeared complicated with more signals than expected in the aryl region. A more detailed analysis revealed that signals in the 5.9-8.0 ppm region appeared in a set of two, with an integration ratio of 0.6:0.4 per assigned proton, while the number of upfield-shifted signals appear as expected for the complex, with an integration of 1 per assigned proton. This phenomenon was also observed in ¹⁹F spectra, with two peaks appearing at -59.50 and -59.88 ppm, with a concurrent integration ratio of 0.6:0.4. The complementary integration between the down- and upfieldshifted protons suggests dynamic behavior in the solution of the complex, which is associated with the two possible isomers of the unsymmetrically substituted BGCF3 ligand (Fig. 1). The ligand has two available N-binding sites, which result in two possible regioisomers: A and B (Fig. 1).

A series of varied-temperature NMR experiments were performed for the title complex in acetone-d₆ (at 50 °C) or upon cooling DCM-d₂ solution to -40 °C (Fig. S3 and S4, ESI†). However, no change was observed in the NMR spectra; for instance, the signals shifted by the same degree on cooling for each set, but the integration ratio of 0.6:0.4 was maintained. To further verify this, we isolated the single crystals of the title **PCCP**

Fig. 1 Molecular and crystal structures of the carbene metal amide BICAuBGCF3 (left) with key structural parameters. Ellipsoids are shown at 50% probability with hydrogen atoms omitted for clarity. Molecular structure of the two possible isomers (right).

complex with confirmed A geometry (Fig. 1) and dissolved them in DCM-d² again to run ¹H NMR spectra from the single crystals to confirm the presence of a single isomer. However, the NMR spectra demonstrated two sets of peaks with an integration ratio of 0.6:0.4, confirming the presence of isomerism in the fluid media. Our previous works demonstrated fluxional behaviour in the solution for copper-based CMA complexes with formamidinato and guanidinato ligands, where the (CAAC)Cufragment experienced a dynamic exchange between the two N-binding sites of the amido ligand.²⁶ Interestingly, BG-CMA complexes with the methoxy-substituted benzoguanidinato ligand have been reported as a single isomer, which is likely associated with the electron-donating nature of the methoxy substituent preferentially stabilising one isomeric form, A. The theoretically calculated energy difference between the two isomers A and B is 2.55 kJ mol⁻¹, where isomer A is energetically more favourable than isomer B.

The molecular structure of BICAuBGCF3 was confirmed using single crystal X-ray diffraction, as shown in Fig. 1. We checked multiple single crystals and found only a single isomer A. The gold complex shows a linear two-coordinate geometry around the central gold atom with the C-Au-N angle at nearly 180°. The torsion angle between BIC carbene (N1-C1) and amide ligands (N2-C25) is 18.4(6)°, which is similar to that of complex Au2. The Au-N bond length is the same as that for the unsubstituted complex Au2, while the Au-C bond length is approximately 0.04 Å longer for BICAuBGCF3 than that for Au2. This structural difference results in a 0.04-Å larger separation (C1···N2 distance) between donor and acceptor ligands for BICAuBGCF3, thus impacting its photophysical properties, vide infra.

Electrochemical properties

The redox behaviour of the title gold complex was analysed in THF solution using ["Bu₄N]PF₆ as the supporting electrolyte

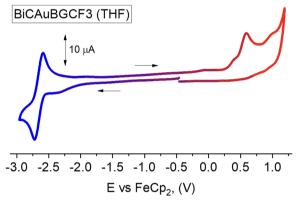


Fig. 2 Full-range cyclic voltammogram for the BICAuBGCF3

(Fig. 2); the electrochemical data are summarised in Table 1. The BICAuBGCF3 complex shows a quasi-reversible reduction process at -2.66 V, which is close to that of the analogous unsubstituted **Au2** complex (-2.78 V). This results in a 0.1-eV more stabilised LUMO energy level for the title complex (-2.83 eV)compared with Au2 (-2.69 eV). The BICAuBGCF3 complex shows an irreversible oxidation process at +0.59 V, which is 0.27 V anodically shifted compared with the analogous Au2 complex (Table 1). This suggests that the electron-withdrawing CF₃ group stabilises the HOMO energy level for the title complex (-5.8 eV)compared with Au2 (-5.53 eV), similar to the reported CF3-CMA complexes (Scheme 1).20 Overall, the CF3 substituent results in a wide energy gap of 0.14 eV for the title complex, thus implying blue-shifted luminescent properties, vide infra.

Photophysical properties and theoretical calculations

The UV-vis absorption spectra for BICAuBGCF3 were measured in cyclohexane, toluene, THF and dichloromethane solvents (Fig. 3). The complex shows high energy absorption bands in

Table 1 Formal electrode potentials (peak position E_p for irreversible and $E_{1/2}$ for quasi-reversible processes (*), V, vs. FeCp₂), onset potentials (E, V, vs. FeCp₂), peak-to-peak separation in parentheses for quasi-reversible processes ($\Delta E_{\rm p}$ in mV), $E_{\rm HOMO}/E_{\rm LUMO}$ (eV) and band gap values (ΔE , eV) for the investigated BICAuBGCF3 complex and BICAuBG (Au2)^{25a} analogue^a

	Reduction			Oxidation				
	$E_{ m 1st}$	$E_{ m onsetred}$	E_{LUMO} , eV	$E_{1\mathrm{st}}$	$E_{ m onsetox}$	E_{2nd}	E_{HOMO} , eV	ΔE , eV
BiCAuBG ^{25a}	-2.78 (161)	-2.70	-2.69	0.28	0.14	_	-5.53	2.83
BiCAuBGCF3 ^b	-2.66(130)	-2.56	-2.83	0.59	0.41	1.00	-5.80	2.97

^a In THF solution, recorded using a glassy carbon electrode, concentration = 1.4 mM, supporting electrolyte ["Bu₄N][PF₆] (0.13 M), measured at 0.1 V s⁻¹. In THF solution, recorded using a glassy carbon electrode, concentration = 1.4 mM, supporting electrolyte ["Bu₄N][PF₆] (0.13 M), measured at 0.1 V s⁻¹. $E_{\text{HOMO}} = -(E_{\text{onset ox Fc/Fc+}} + 5.39) \text{ eV}$; $E_{\text{LUMO}} = -(E_{\text{onset red Fc/Fc+}} + 5.39) \text{ eV}$.

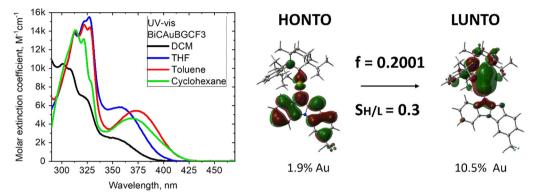


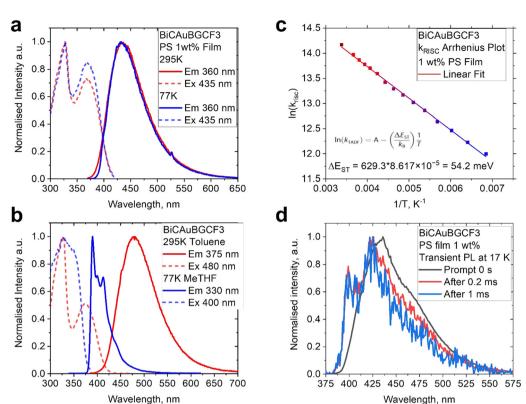
Fig. 3 UV-vis spectra for the BICAuBGCF3 complex in various solvents at 295 K and pertinent frontier orbitals involved in the lowest energy absorption band.

the range from 300 to 345 nm, ascribed to the intraligand π - π * (IL) transitions of the benzoguanidinato and carbene ligands. A broad low-energy band spanning over a wide range from 325 to 425 nm was assigned to a ligand-to-ligand charge transfer L(M)LCT (M = Au) transition from the benzoguanidinato ligand to the carbene ligand. The assignment is consistent with the analogous complex Au2 (Scheme 1), with the lowenergy absorption bands being 25 nm blue-shifted for BICAuBGCF3, thereby reflecting the wider energy gap due to the electron-withdrawing nature of the CF3 substituent and is in agreement with the electrochemistry results. The CT nature of the low-energy absorption band is supported using TD-DFT theoretical calculations, indicating 97% HOMO -> LUMO transition (Fig. 3 and Table S1, ESI†), with 1.9% contribution of the gold orbitals to HOMO and 10.5% to LUMO. Increasing the solvent polarity from cyclohexane to dichloromethane results in a 20-nm blue-shift of the L(M)LCT band (Fig. 3), while the IL band shows little influence from solvent polarity. This is characteristic of CMA materials, which tend to show negative solvatochromism for the low-energy CT band. 18b There is a significant difference between the ground-state dipole moment of the title complex (15.8 D) and that of the unsubstituted complex Au2 (11.6 D). This is a result of the CF₃ electron withdrawing group polarizing the amide donor ligand. The dipole moment for the first singlet excited state for **BICAuBGCF3** having an opposite direction is higher (-3.5 D)(Table S2, ESI†) than that for the **Au2** complex (-6.0 D). ^{25a} The increase in the transition dipole moment of the BICAuBGCF3

complex agrees with its higher oscillator strength coefficient (0.2001) (f, Table S4, ESI† and Fig. 3) compared with Au2 (0.1897). This can be explained by f being directly proportional to the squared value of the transition dipole moment $(|\mu_{S1\to S0}|^2)^{28}$

Photoluminescence properties of the BICAuBGCF3 complex are presented in Fig. 4, and the data collected together with the analogous unsubstituted complex Au2 are presented in Table 2. The complex emits deep-blue light at 432 nm when doped in polystyrene (PS) matrices at 1 wt% doping concentration (Fig. 4). The emission profile is broad and unstructured, indicating that the emission originates from a CT excited state. The emission profile is 34 nm blue-shifted from λ_{max} at 466 nm for Au2. This fact is in line with the 0.15 eV larger band gap for BICAuBGCF3, as measured via electrochemistry and UV-vis and predicted through theoretical calculations, vide infra. The PLQY of BICAuBGCF3 is 60%, which is lower than 92% for the analogous Au2 complex. At 295 K, the BICAuBGCF3 complex shows a remarkably short sub-microsecond excited state lifetime (τ) with a monoexponential decay of 423 ns, which is similar to that for Au2 (406 ns). Therefore, the title complex possesses a high radiative rate of up to $1.4 \times 10^6 \text{ s}^{-1}$ in amorphous PS films.

In toluene, the BICAuBGCF3 complex emits a blue light at 478 nm, which is 34 nm blue-shifted compared with Au2. However, the solution PLQY value drops to 43% for the title complex, while it drops to near unity for Au2. This is likely associated with the dynamic behaviour in the solution



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Fig. 4 Excitation and emission spectra for the gold complex BICAuBGCF3 at 298 and 77 K in 1 wt% polystyrene (PS) films (a), toluene solution and frozen MeTHF glass (b); Arrhenius plot to estimate ΔE_{ST} (c); prompt and delayed (after 0.2 and 1 ms) luminescence profiles at 17 K for the 1 wt% PS film (d).

Table 2 Photophysical properties of the BiCAuBGCF3 and analogous unsubstituted Au2 complexes in various matrices

	λ _{em} (nm)	τ (ns)	Φ (%) ^a	$k_{\rm r} (10^6 \; {\rm s}^{-1})^b$	$k_{\rm nr} (10^5 {\rm s}^{-1})^c$	$CT/LE (eV)^d$	λ_{em} (nm, 77 K)	τ (μs, 77 K)
Toluene solution Au2	511	493	100	2.03	_	MeTHF frozen solution 2.77/3.29 414 26.5 (95.		
BiCAuBGCF3	478	240	43	1.79	23.8	3.01/3.25	390	239 (4.84%) 150 (9.81%) 625 (45.16%) 1960 (45.03%)
1 wt% PS film Au2	466	406	92	2.27	1.97	2.99/—	456	23.5 (46.2%)
BiCAuBGCF3	432	423	60	1.42	9.46	3.17/3.23	432	41.2 (53.8%) 23.9 (90.2%) 258 (9.8%)

^a Quantum yields determined using an integrating sphere. ^b Radiative rate constant $(k_r) = \Phi/\tau$. ^c Nonradiative constant $(k_{nr}) = (1 - \Phi)/\tau$. In case of two-component lifetime (τ) , an average was used: $\tau_{av} = (B_1/(B_1 + B_2))\tau_1 + (B_2/(B_1 + B_2))\tau_2$, where B_1 and B_2 are the relative amplitudes for τ_1 and τ_2 , respectively. d CT/LE energies based on the onset values of the emission spectra blue edge at 77 K.

compared with in the solid state, vide supra. The lower PLQY values and shorter emissive lifetime in toluene at 240 ns result in a dominating non-radiative decay rate of 2.38×10^6 s⁻¹, thus indicating energy losses for the title complex in the fluid media.

Theoretical calculations confirm the first CT nature for the S₁ state and the large energy difference of 0.82 eV to the second CT singlet S₂ state (Table S4, ESI†). This significant energy separation validates our focus on the S₁ state for understanding the photophysical behaviour of the title complex, which is in a good agreement with the experimental observations.²⁹ We previously established that faster TADF is observed for

CMA complexes with a locally excited triplet (³LE) state being significantly higher in energy than the CT state. 25a This inhibits the parasitic, long-lived phosphoresce contribution from the ³LE state. At 77 K in MeTHF, the emission profile becomes highly vibronically resolved with an emissive lifetime in the millisecond regime at 1.18 ms (Table 2). This vibronically resolved profile is ascribed to the phosphorescence from the higher-lying ³LE state. TDDFT calculations demonstrate that ³LE state is localised on the BGCF3 ligand and originates from the HOMO \rightarrow LUMO+3 (59%) and HOMO \rightarrow LUMO+4 (20%) transitions. High-energy onsets at 298 K in toluene and frozen

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MeTHF glass at 77 K revealed an energy of 3.01 eV for CT and 3.25 eV for 3LE states with an energy difference of 0.24 eV for $\Delta E(\text{CT}^{-3}\text{LE})$. This is lower than the $\Delta E(\text{CT}^{-3}\text{LE})$ for the **Au2** complex (0.52 eV); however, it is well above the CT manifold by 0.2 eV. The high energy of the ³LE state of the benzoguanidinato derivative, despite having electron withdrawing CF₃ substituents, allows the occurrence of efficient and fast TADF. This work demonstrates that electron-withdrawing substituents on the benzoguanidinato ligand core are an excellent strategy for tuning the luminescence of TADF CMA emitters to afford deepblue emission. However, symmetric ligands should be used to avoid isomerism, which can likely lead to reduced PLQY values for the title complex compared with the Au2 compound.

Another prerequisite for highly efficient CMA TADF is a small exchange energy between the singlet and triplet excited states (ΔE_{ST}). We previously reported that the Au2 complex exhibits a very small reverse intersystem crossing (rISC) activation energy (ΔE_a) value of 56 meV. Herein, variable-temperature lifetime measurements were conducted to investigate the ΔE_a for the title complex BiCAuBGCF3. Upon cooling, the PL profile remains broad and unstructured (Fig. 4), while the emissive lifetime increases to the microsecond regime up to 46.8 µs, which is 100-fold longer compared with the room temperature value (Table 2). The ΔE_a for **BiCAuBGCF3** was estimated using an Arrhenius plot at varied temperatures with $\ln k_{\rm RISC}$ vs. 1/T to afford 54 meV, which is comparable with 56 meV for the Au2 complex, thus supporting the rapid radiative rate of TADF. Overall, the title complex possesses the required fast and deepblue TADF luminescence regardless of the fact that it exists as a mixture of two isomers in fluid media. We were unable to isolate and characterize the isomer B for the BiCAuBGCF3 complex in the solid state; however, our theoretical calculations predict a very similar photoluminescence behavior compared with the isolated isomer A (Tables S1-S5, ESI†).

The PS film of the BiCAuBGCF3 complex exhibited a broad CT luminescence profile (Fig. 4d, black profile) even at 17 K, while the transient photoluminescence experiment revealed the presence of ³LE states (Fig. 4d, red profile after a delay of 0.2 ms) with a clear vibronic structure. This experiment enabled us to determine that the energy gap $\Delta E(CT^{-3}LE)$ is -0.06 eV in the PS film, which is considerably smaller compared with that in the fluid media (-0.24 eV) (Table 2, see MeTHF data). Such a large difference reflects a highly polar nature of the CMA material, i.e. lower the polarity of the media, greater the destabilization of the CT state (blue-shift in luminescence).

Conclusion

We prepared and fully characterised a gold(1)-based CMA complex with BiCAAC-carbene and a novel benzoguanide ligand having electron-withdrawing CF₃ substituent. The asymmetric substitution of the ligand affords two possible isomers of the gold CMA material BICAuBGCF3 complex, which were observed using ¹H and ¹³F NMR spectroscopy. In the solid state, the complex exists in a form where (carbene)gold(I) and CF3

moieties are located on the opposite sites of the benzindole ring of the ligand L. Such a CF3-substituted BG-CMA material possesses a stabilised HOMO energy level shifted by 0.27 eV, leading to a wider HOMO-LUMO gap and deep-blue emission compared with the unsubstituted BG-CMA material. This isomerism leads to reduced quantum yields (43%) and a pronounced non-radiative decay process with a rate of up to 2 \times 10^{-6} s⁻¹ in fluid media. The title complex avoids parasitic phosphorescence from the amide-based ³LE state, demonstrating that electron-withdrawing substitution at the benzoguanidinato amide ligand is a good strategy for achieving optimal deep-blue thermally activated delayed fluorescence at 432 nm in polystyrene films. The BICAuBGCF3 complex possesses bright PLQY values of up to 60% with rapid radiative rates of up to $1.42 \times 10^{-6} \text{ s}^{-1}$. Future studies should use symmetric benzoguanidinato ligands to improve PLQY values up to unity by reducing non-radiative pathways to prevent dynamic isomerism processes.

Author contributions

A. B. performed the synthesis, steady-state photoluminescence and electrochemistry studies. A. S. R. performed X-ray crystallography. N. L. P. and M. L. carried out theoretical calculations and data analysis. A. S. R. and M. L. planned the project and designed the experiments. A. B. and A. S. R. co-wrote the manuscript. All the authors contributed to the discussion of the results, analysis of the data and review of the manuscript.

Conflicts of interest

The authors declare no competing interests.

Data availability

The data supporting this article have been included as part of the ESI.†

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