Fernandez-Cestau J, Bertrand B, Blaya M, Jones G, Penfold TJ, Bochmann M. 

**Synthesis and Luminescence Modulation of Pyrazine-Based Gold(III) Pincer Complexes.**

*Chemical Communications* (2015)  
DOI: 10.1039/C5CC07523H

Copyright:  
This article is licensed under a [Creative Commons Attribution 3.0 Unported Licence](http://creativecommons.org/licenses/by/3.0/).

Link to published article:  
[http://dx.doi.org/10.1039/C5CC07523H](http://dx.doi.org/10.1039/C5CC07523H)

Date deposited:  
02/10/2015

This work is licensed under a [Creative Commons Attribution 3.0 Unported License](http://creativecommons.org/licenses/by/3.0/).
Synthesis and luminescence modulation of pyrazine-based gold(III) pincer complexes†

Julio Fernandez-Cestau, Benoit Bertrand, Maria Blaya, Garth A. Jones, Thomas J. Penfold* and Manfred Bochmann*†

The first examples of pyrazine-based gold(III) pincer complexes are reported; their intense photoemissions can be modified by protonation, N-alkylation or metal ions, without the need for altering the ligand framework. Emissions shift from red (77 K) to blue (298 K) due to thermally activated delayed fluorescence (TADF).

Gold(III) complexes with bis-cyclometallated ligands are characterized by their chemical stability and resistance to reduction. The ligand scaffold based on 2,6-diphenylpyridine has proved particularly useful in gold(III) chemistry and forms (C^N^C)AuX pincer complexes of type A (Chart 1). Such complexes have proved to be highly versatile and, in combination with strong carbon-based σ-donor ligands (e.g. X = N-heterocyclic carbene, alkynyl), display interesting photophysical properties. This C^N^C-C ligand system has also been successful in stabilizing types of compounds that have frequently been invoked as unstable intermediates in catalytic cycles or postulated in computer modeling of catalytic processes, such as gold(III) hydrido, alkene, CO and peroxo complexes.

Photoemissive materials as components of electronic devices such as flat screen displays should ideally be capable of covering the whole range of the visible spectrum. Such changes in emission colours can be induced by suitable modification of the ligand framework. For (C^N^C)Au(III) complexes a widely applied strategy for modulating the photoluminescence (PL) response and widening the range of emission wavelengths has been the introduction of electron donating or withdrawing substituents in the 4-position of the pyridine moiety. There are however limitations in this approach: firstly, the synthesis of C^N^C gold complexes involves two C–H activation steps, each of which is sensitive to the ligand structure and needs to be optimized for each new ligand; secondly, the modulation of electronic characteristics of the central pyridine moiety that can be achieved by inductive or mesomeric substituent effects is limited.

Rather more profound electronic changes in C^N^C ligands can be introduced by replacing the central pyridine ring by other heterocycles, such as pyrazine, to give compounds of type B. The lowest-energy π–π* transition in pyrazine is about 0.95 eV smaller than in pyridine, therefore pyrazine ligands are therefore much better electron acceptors and are likely to produce a red-shift of their UV and photoemission wavelengths. In addition, pyrazine complexes B offer scope for further derivatisation by protonation or quaternisation of the non-coordinating N atom, to give salts of type C.

Complexes of aryl-substituted pyrazines and quinoxalines are of course well-known for iridium(III) and platinum(III), since for these metals they are readily accessible by direct cyclometallation of the neutral ligand precursors by noble metal halides. By contrast, related gold(III) complexes have until now been inaccessible since the usual methods employed for the synthesis of pyridine complexes A fail for the analogous pyrazine derivatives. Here we report the first examples of cyclometallated Au(III) pyrazine complexes and the facile modification of their photoluminescence properties.

The mercuration of the pro-ligand 2,6-bis(4-tert-butylphenyl)pyrazine (pz) requires forcing conditions but proceeds using Hg(tfa)2 in Htfa (tfa = CF3CO2) to give (C^N^C^N^C)HgCl 2Htfa (1). Transmetallation with KAuCl4 affords (C^N^C^N^C)AuCl (2) as a yellow crystalline powder in good yield (Scheme 1).

† Electronic supplementary information (ESI) available: Details of synthesis and characterization, X-ray crystallography, photophysical properties, theoretical calculations. CCDC 1417819–1417822. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc07523h

[Image: Chart 1: Structures A, B, and C]

* School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, UK. E-mail: m.bochmann@uea.ac.uk
† Department of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK. E-mail: Tom.Penfold@newcastle.ac.uk
‡ Electronic supplementary information (ESI) available: Details of synthesis and characterization, X-ray crystallography, photophysical properties, theoretical calculations. CCDC 1417819–1417822. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc07523h
Substitution of the chloride ligand in 2 with KCN gives the cyanide complex 3, while treatment with dimethylpyrazole affords the pyrazolato complex 4. The reaction with AgC≡CR in CH₃CN affords the acetylides (C≡Npz≡C)AuC≡CR (5a, R = Ph; 5b, R = Bu≡C) in essentially quantitative yield.

Pyrazine is only weakly basic (pKa 1.30, vs. 5.20 of pyridine). However, protonation of 2 by HBF₄Et₂O generated the corresponding salt 6. Remarkably, the protonation by dry HCl in Et₂O proved to be reversible, and evaporation of the solvent from the HCl adduct regenerated neutral 2. The alkylation of the non-coordinating pyrazine N-atom was achieved using Meerwein’s salt [Me₃O]BF₄ to give 7 (Scheme 1) as a deep-red crystalline solid in 87% yield. The molecular structures [selected bond distances (Å) and angles (°)] of 7: Au–N1 1.972(3), Au–Cl 2.2651(11), Au–C4 2.078; N1–Au–C4 81.28(8), C4–Au–Cl 98.72(8), C4–Au–C25 99.3(3), C16–Au–C25 99.0(3), C6–Au–C16 161.6(3), Au–C25–C26 175.9(6), C25–C26–C27 177.4(7).

Scheme 1

Conditions: (i) KAuCl₄, CH₃CN/H₂O 1 : 1, reflux 72 h. (ii) KCN, CH₃CN/H₂O, 20 °C, 24 h. (iii) KO[Bu₃]BF₄, toluene/1,2-C₆H₄F₂ (5 : 1 v/v), 20 °C, 30 min. (iv) HBF₄Et₂O, Et₂O, 20 °C, 30 min. (v) [Me₃O]BF₄, toluene/1,2-C₆H₄F₂ (5 : 1 v/v), 12 h. (vi) Me₃O, 20 °C, 24 h. (vii) AgC≡CR, CH₃CN/H₂O, 20 °C, 24 h. (viii) HBF₄Et₂O, Et₂O, 20 °C, 30 min. (ix) [Me₃O]BF₄, toluene/1,2-C₆H₄F₂ (5 : 1 v/v), 12 h.

The pyrazine ligand framework of type B therefore significantly widens the range of photo emissive metal–ligand combinations.

In solution, the neutral complexes 2–5 all emit in the yellow to green region of the spectrum, mainly due to a triplet state based on the diphenylpyrazine pincer ligand. The excited state lifetimes show biexponential decay, with the fast component in the range of 5–20 ns.

At 77 K the emissions of 2, both in the solid state (λ_max = 563 nm) and in solution (λ_max = 532 nm), agree reasonably well with the value calculated for a T¹ → S⁰ transition (λ_calc = 541 nm). However, at 298 K the emission shows a significant blue-shift, to 482 nm, a feature that is even more pronounced on addition of acid (vide infra).

One of the most important challenges in the design of photoluminescent devices is the ability to modulate the energy of the emitted light. In the pyrazine ligand system, the easiest way to achieve this is by making use of the non-coordinating nitrogen of the pyrazine ring. Strong Brønsted and Lewis acids do indeed produce dramatic changes in PL response. In order to eliminate any possible anion effects, initial protonation studies were carried out using the solid Brønsted acid [H(ΟEt₂)₃][H₂N{B(C₆F₅)₃}] (”HNB₂”). As shown in Fig. 1a, protonating 2 with this acid results in a blue-shift compared with the neutral complex, from 482 to 458 nm. On the other hand, at 77 K the emissions of both the neutral and protonated compounds are remarkable similar (as expected since both the HOMO and LUMO are based on the pyrazine ligand and are equally affected by protonation) and the emission is due to an intra-ligand charge transfer (ILCT) process.
The temperature-dependence of the photoluminescence response is in agreement with a TADF process, where the energy difference between the T₁ and S₁ excited states is with this, solutions of 5a (CH₂Cl₂, 1 × 10⁻⁴ M) in the absence and presence of two equivalents of [H(OEt₂)₂][H₂N{B(C₆F₅)₃}²] (HNB₂) at 298 and 77 K. (b) PL response of 5a (CH₂Cl₂, 1 × 10⁻⁴ M) to the addition of HOTf at 298 K. (c) PL of mixtures of 5a with equimolar amounts of MCl₂ (M = Zn, Cd, Hg) in THFMe-2 ([5a] = 10⁻⁴ M) at 298 K. (d) PL response of 5a (THFMe-2, 5 × 10⁻⁴ M) to the addition of AgOTf at 77 K (top) and 298 K (bottom).

The modulations of the TADF properties of 5a by the addition of cations can be explained in terms of an intermolecular interaction which prevents the overlap of the TADF and phosphorescence transitions. This effect can be rationalized by considering the steric repulsion between the pyrazine-N atom and the H₂N{B(C₆F₅)₃}²⁺ cations, which prevents the formation of aggregates. As a result, the addition of AgOTf or CuOTf enhances the TADF emission at 77 K, while the addition of HOTf leads to a decrease in the TADF emission at 298 K. These effects are consistent with the TADF mechanism, as which are characterized by a band maximum at 545 nm. The mixture of 5a with two equivalents of Ag⁺ both show the same emission band, while 1 equivalent of Ag⁺ gives two bands of about equal intensity. For these reasons, we tentatively suggest the formation of an aggregate of 5a with two Ag⁺ ions (e.g. coordination of two Ag⁺ ions to the C≡C bond and the pyrazine-N atom may be envisaged).

The N-methylated complex 7 mirrors the behaviour of the H⁺ adducts and shows blue emission in solution (£em = 460 nm) but is dark-red in the solid state (£em = 623, 680sh).

In summary, cyclometallated gold(iii) pincer complexes based on pyrazine provide a new family of photoluminescent compounds which allow facile modulation of the emission characteristics by protonation, alkylation, Lewis acids or metal ions, without the need for modifying the pincer ligand framework. The modulation arises from the coexistence of high energy TADF and 3IL (C≡Npz≡C)/3LLCT (X → C≡Npz≡C) transitions.

This work was supported by the European Research Council. M. B. is an ERC Advanced Investigator Award holder (grant no. 338944-GOCAT).

Notes and references

1. K.-H. Wong, K.-K. Cheung, M.-W. Chan and C.-M. Che, Organometallics, 1998, 17, 3505.
2. Reviews: (a) C. Bronner and O. S. Wenger, Dalton Trans., 2011, 40, 12409; (b) V. W.-W. Yam and K. M. C. Wong, Chem. Commun., 2011, 47, 11579.
3. (a) V. K.-M. Au, D. P.-K. Tsang, Y.-C. Wong, M.-Y. Chan and V. W.-W. Yam, J. Organomet. Chem., 2015, 792, 109; (b) M.-C. Tang, D. P.-K. Tsang, Y.-C. Wong, M.-Y. Chan, K. M.-C. Wong and V. W.-W. Yam, J. Am. Chem. Soc., 2014, 136, 17861 and cited refs.
4. (a) G. Cheng, K. T. Chan, W.-P. To and C.-M. Che, Adv. Mater., 2014, 26, 2540; (b) W.-P. To, K. T. Chan, G. S. M. Tong, C. S. Ma, W.-M. Kwok, X. G. Guan, K. H. Low and C.-M. Che, Angew. Chem., Int. Ed., 2015
This journal is © The Royal Society of Chemistry 2015

5 (a) D.-A. Roșca, D. A. Smith, D. L. Hughes and M. Bochmann, Angew. Chem., Int. Ed., 2012, 51, 10643; (b) N. Savjani, D.-A. Roșca, M. Schormann and M. Bochmann, Angew. Chem., Int. Ed., 2013, 52, 874; (c) D.-A. Roșca, J. A. Wright, D. L. Hughes and M. Bochmann, Nat. Commun., 2013, 4, 2167; (d) D.-A. Roșca, J. Fernandez-Cestau, J. Morris, J. A. Wright and M. Bochmann, Sci. Adv., 2015, in press.

6 C. Walker, M. H. Palmer and A. Hopkirk, Chem. Phys., 1989, 141, 365.

7 I. C. Walker and M. H. Palmer, Chem. Phys., 1991, 153, 169.

8 See for example: (a) S. H. Wu, S. E. Burkhardt, J. Yao, Y. W. Zhong and H. D. Abruna, Inorg. Chem., 2011, 50, 3959; (b) V. N. Kozhevnikov, M. C. Durrant and J. A. G. Williams, Inorg. Chem., 2011, 50, 6304; (c) S. Culham, P.-H. Lanoe, V. L. Whittle, M. C. Durrant, J. A. G. Williams and V. N. Kozhevnikov, Inorg. Chem., 2013, 52, 10992; (d) P.-H. Lanée, C.-M. Tong, R. W. Harrington, M. R. Probert, W. Clegg, J. A. G. Williams and V. N. Kozhevnikov, Chem. Commun., 2014, 50, 6831.

9 H. J. Sosćun Machado and A. Hinchliffe, THEOCHEM, 1995, 339, 255.

10 S. J. Coles and P. Gale, Chem. Sci., 2012, 3, 683.

11 D.-A. Roșca, D. A. Smith and M. Bochmann, Chem. Commun., 2012, 48, 7247.

12 S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. L. Hughes and M. Bochmann, Organometallics, 2002, 21, 451.

13 Reviews: (a) H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, Coord. Chem. Rev., 2011, 255, 2622; (b) Y. Tao, K. Yuan, T. Chen, P. Xu, H.-H. Li, R. F. Chen, C. Zheng, L. Zhang and W. Huang, Adv. Mater., 2014, 26, 7931.

14 (a) M. J. Leitl, V. Krylova, P. I. Djurovich, M. E. Thompson and H. Yersin, J. Am. Chem. Soc., 2014, 136, 16032; (b) V. A. Krylova, P. I. Djurovich, B. L. Conley, R. Haiges, M. T. Whited, T. J. Williams and M. E. Thompson, Chem. Commun., 2014, 50, 7176; (c) R. Marion, F. Sguerra, F. Di Meo, E. Sauvageot, J.-F. Lohier, R. Daniellou, J.-L. Renaud, M. Linares, M. Hamel and S. Gaillard, Inorg. Chem., 2014, 53, 9181.