Prayogik Rasayan

C,N,C Pincer Complexes of Gold(III): Organometallic Chemistry, Liquid Crystals, Photophysics and OLEDs

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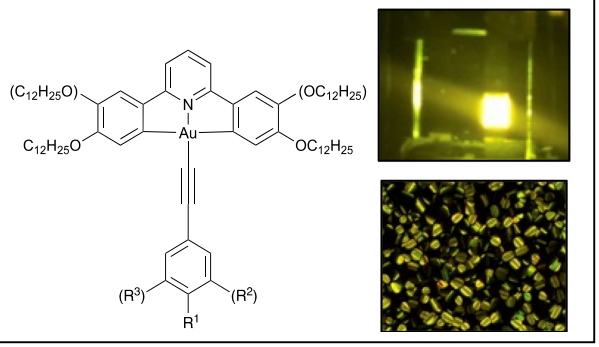
Abstract

Owing to their ability to promote efficient spin-orbit coupling, complexes of iridium(III), platinum(II) and, latterly, gold(III), have attracted attention as the emissive components in OLED displays. Making such complexes liquid crystalline offers some potential advantages and, while liquid-crystalline complexes of iridium(III) and platinum(II) are quite well studied, those of gold(III) are much newer. The preparation and properties of come of these gold(III) complexes are considered.

Keywords: *Gold(III); Metallomesogen; OLED; Liquid Crystal*

Graphical abstract



1. Introduction

While presently there is much effort directed towards thermally activated delayed fluorescence (TADF) as a mechanism to allow the deployment of organic-only emitters in OLED displays,[1] the ability to harvest both singlet *and* triplet excitons has for some time relied on the enhanced spin-orbit coupling possible in complexes of heavy transition metals. Iridium has long been favoured for application,[2] but the photophysical properties of platinum(II) complexes have created significant interest in these materials, too.[3]

Our own interest here has been in realising multifunctional materials by conferring liquid crystal properties on complexes of these metals. As we and others have shown, this is non-trivial when octahedral iridium(III) is concerned as the three-dimensional nature of the complexes is not so readily compatible with the anisotropy needed to realise liquid crystal mesophases (Fig. 1).[4-8]Nonetheless, examples have been realised with very respectable PLQY values.

In terms of forming liquid crystals, the square-planar geometry of platinum(II) is a much better prospect and examples exist where both calamitic (rod-like)[9,10] and discotic (disk-like) complexes have been prepared,[11] exhibiting nematic and smectic phases (calamitic materials) or columnar phases (discotics). The complexes have been designed either to be inherently anisotropic by virtue of the ligand design with flexible alkyl chains, or by decorating the emissive chromophore with groups capable of conferring liquid crystallinity. Both approaches have also been used with platinum(II) and examples of materials are given in Fig. 2 noting that work in both mesogenic platinum(II) and iridium(III) emitters has been reviewed.[12]

More recently and following the initial work of Yam and co-workers,[13] gold(III) complexes, formally isoelectronic with platinum(II), are being studied with some impressive results from both photoluminescence quantum yields (PLQY) and device-based external quantum efficiencies (EQE).[14] Being also square planar, they are highly amenable to functionalisation to create discotic mesogens and this article gives an overview of the work we have carried out in this regard.

2. Experimental

Experimental details relating to the materials discussed in this manuscript are found in the original papers.[15-18]

3. Result and discussion

Synthesis – 1: The synthesis of the complexes is shown in Scheme 1.[15] Thus, boronic acids derived from 4-methoxybenzene or 3,4-dimethoxybenzene are cross coupled with 2,6-dibromopyridine to give the precursor (**1**), which is then demethylated and re-alkylated using 1-bromododecane yielding ligand (**2**). This is then reacted with mercury(II) acetate and, following workup with aqueous lithium chloride, an intermediate chloromercury(II) complex (**3**) is obtained in low yields as an impure, grey solid. This can be reacted with $[AuCl_4]^-$ to give the chlorogold complex (**4**)

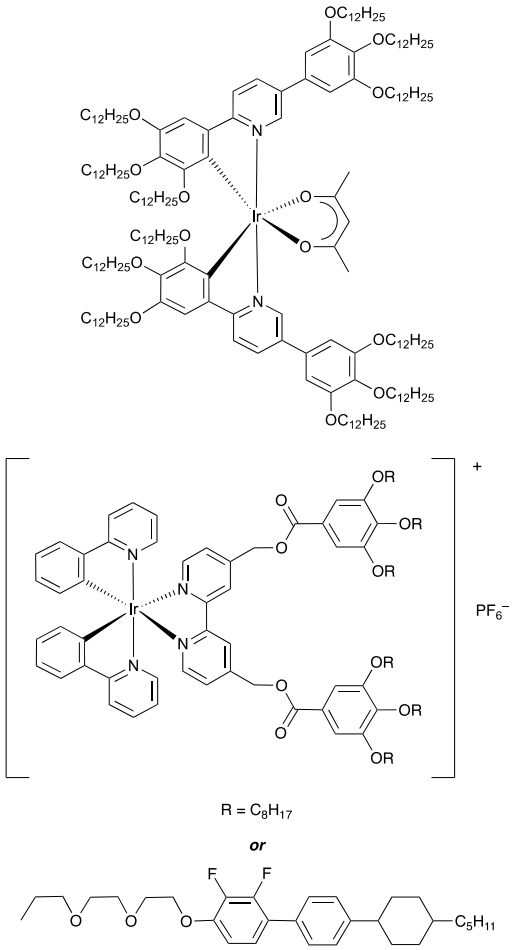


Figure 1 Emissive, liquid-crystalline complexes of iridium(III).

from which the final product (**5-12**) is obtained *via* a copper-mediated coupling to a substituted phenylacetylene. The phenyl group contains between one and three substituents as shown in the Scheme using one of alkyl, alkoxy or 1*H*,1*H*,2*H*,2*H*-perfluoroalkyloxy chains.[16] That the complexes are planar is demonstrated by determination of the single crystal X-ray structure for some examples (*e.g.* in Fig. 3).

Liquid Crystal Properties: As shown in Fig. 4, complexes with four dodecyloxy chains on the pincer ligand show more stable mesophases (and less stable crystal phases) than the equivalents with only two such chains, leading to complexes with mesophase ranges of well over 100 °C in some cases. All complexes in this class, with two exceptions, showed a Col_h phase (Fig. 5) over their entire mesophase range. The introduction of semiperfluorocarbon chains on the phenylacetylene led to a very similar outcome albeit with slightly more stable crystal and liquid crystal phases, with the exception of complex **11f**-10 (*i.e. m* = 10), for which the rather remarkable phase sequence shown below was found:

$$Crys \bullet Col_r^1 \bullet Col_r^2 \bullet N_{Col} \bullet Col_h \bullet Iso$$

Thus, a nematic phase (postulated as a columnar nematic – Fig. 5) was found between two much more ordered phases, namely Col_h and Col_r (the superscripts '1' and '2' represent different Col_r phases).[17] This unusual behaviour was interpreted as arising from the immiscibility of hydrocarbon and fluorocarbon chains and effectively thermally driven

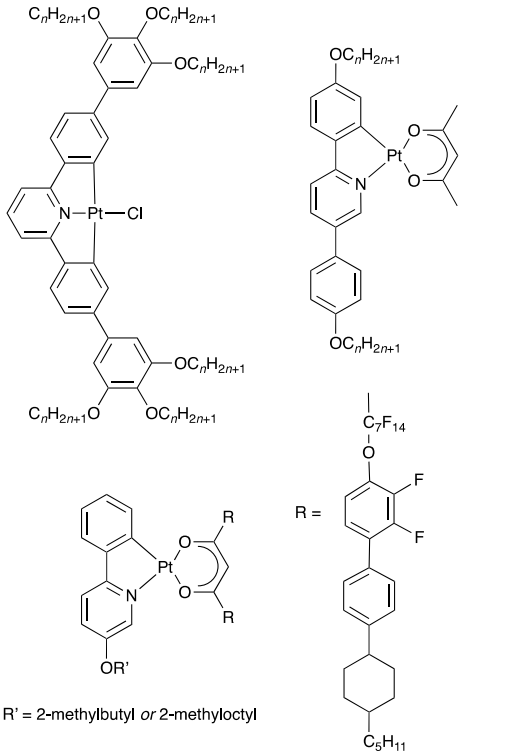


Figure 2 Examples of emissive, liquid-crystalline complexes of platinum(II).

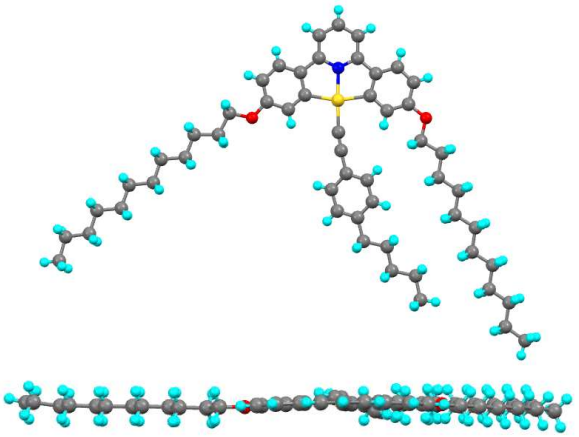
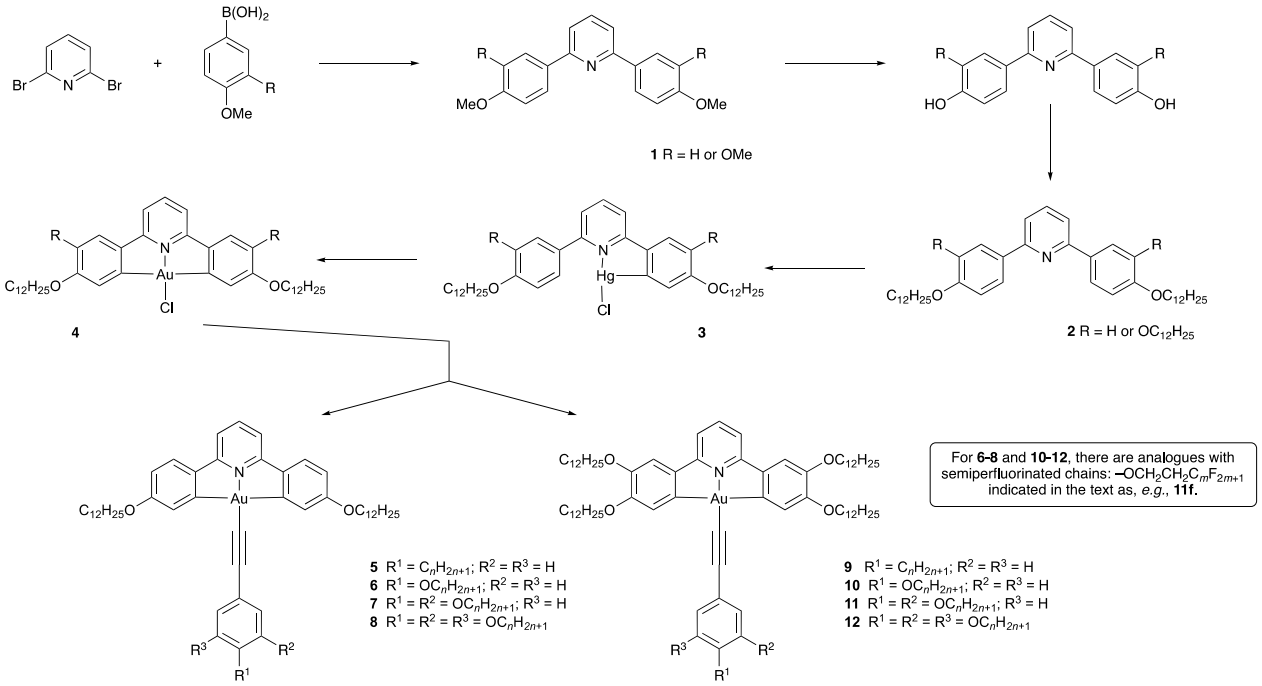


Figure 3 Two views of complex **5**-5 showing the planarity.

consolution. Thus, the 'phase separation' is regarded as significant *below* the N_{Col} phase, while above it, it is overcome by thermal energy allowing the high-symmetry hexagonal phase to form.

Photophysical Properties: The phenylacetylene co-ligand was shown to have very little effect on the solution photophysics and indeed quantum yield depended mainly on the substituted pattern of the pincer ligand, with the complexes bearing the 4,4'-didodecyloxy-substituted ligand showing photoluminescence quantum yield (PLQY) values up to 3.6%, while with the 3,3',4,4'-tetradodecyloxy-substituted ligand, the PLQY were an order of magnitude higher at up to 36%. In the four-chain complexes, the energy of the emissive state is decreased by around 2000 cm^{-1}, thus increasing by the same amount the activation energy required to access



Scheme 1 Synthetic route to the gold complexes.

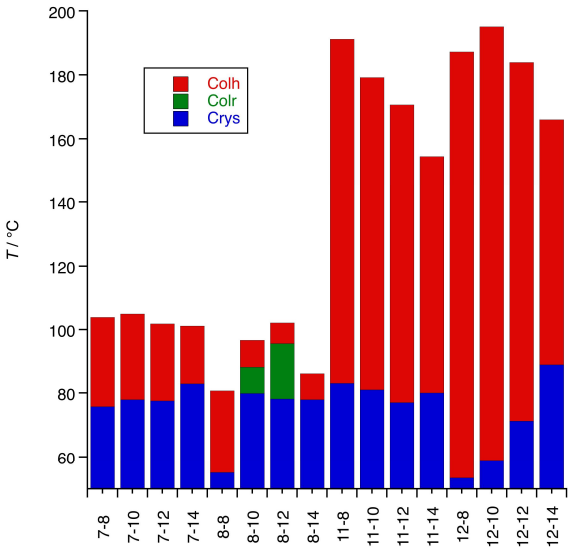


Figure 4 Plot to compare transition temperatures for complexes with two (**7,8**) and four (**11,12**) chains on the pincer ligand.

the deactivating *d-d* states. This cuts off this deactivation pathway as evidenced by a reduction in k_{nr} by almost two orders of magnitude. These values are among the best for complexes of *C,N,C* pincer ligands bound to gold(III).

Device Properties: First of all, the electron mobilities of three complexes with all hydrocarbon terminal chains were evaluated in both the pristine (solid) state and after annealing to give the liquid crystal state. While annealing did not lead to the formation of a columnar monodomain, the presence of columnar domains, along which conductivity will be enhanced, nonetheless led in each case to an enhancement in the measured mobilities.

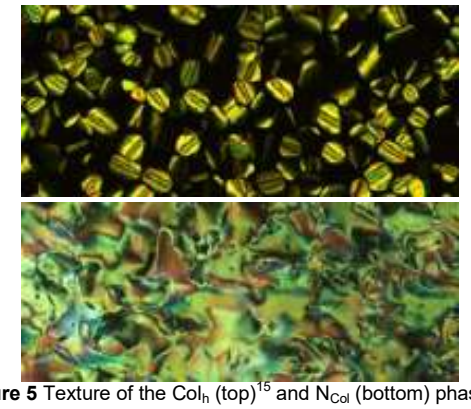


Figure 5 Texture of the Col_h (top)[15] and N_{Col} (bottom) phases.[17]

Devices with a structure (again for the all-hydrocarbon complexes) of (Fig. 6): ITO/PEDOT:PSS/ emitter /DPEPO/TmPyPB/CsF/Al (anode = indium tin oxide; hole injection layer = PEDOT:PSS (poly(3,4-ethylenedioxy-thiophene):polystyrene sulfonate); host = PVK (poly(9-vinylcarbazole)) and OXD-7 (1,3-bis[2-(*t*butyl-phenyl)-1,3,5-oxadiazo-5-yl]benzene); hole/exciton blocking layer = DPEPO (bis[2-(diphenylphosphino)phenyl]ether oxide); electron transport layer = TmPyPB (1,3,5-tris(3-pyridyl-3-phenyl)benzene); electron-injecting layer = caesium fluoride; metal cathode = aluminium) ,were then fabricated to evaluate the electroluminescence properties (Fig. 7). An emitter loading of 5% was determined as optimum in these devices and external quantum efficiencies (EQE) values of between 5.52% and 7.15% were found. These are very respectable for the type of complex under study and, interestingly, there was no relationship between device EQE and solution PLQY.

The same was found when the complexes bearing semiperfluorocarbon chains on the phenylacetylene co-ligand were studied. Having the same pincer ligand, the PLQY values were the same as the materials with all-hydrocarbon

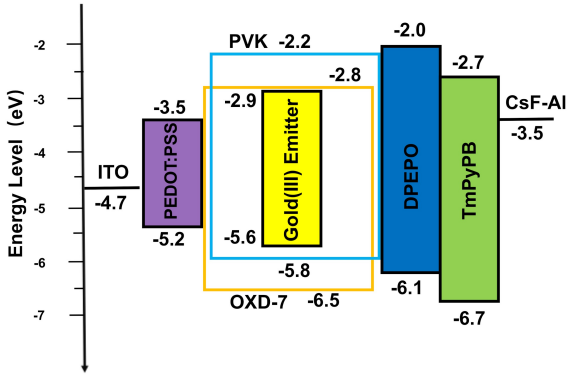


Figure 6 General schematic for the structure of doped-devices with gold(III) emitters (from ref. 15).

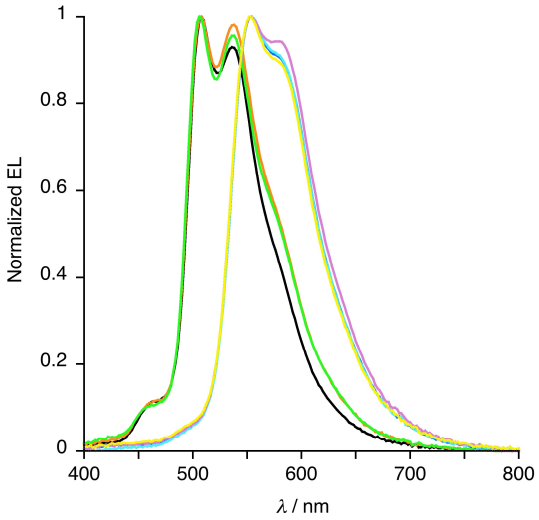


Figure 7 Electroluminescence spectra – complexes **5** and **7** to higher energy, complexes **9-12** to lower energy (from Ref. 15).

chains, but the EQE values were <0.7% (slightly different device components). This was on account of both the very low solubility of the complexes and their tendency to aggregate in the host, both behaviours being driven by the semiperfluorocarbon chains.

***Synthesis – 2*:**

As noted above, realisation of these complexes from the ligand is a two-step synthesis that first requires the preparation of a mercury(II) complex which, after metathesis with $[AuCl_4]^-$, leads to the target gold(III) complexes. Self-evidently, however promising these and related gold(III) complexes may be for application, no commercialisation is possible with a requirement to use mercury in the synthesis.

Direct auration of 2-phenylpyridine-type ligands is notoriously difficult, with some of the best syntheses being described by Tilset and co-workers under conditions of microwave radiation and using either $Au(OAc)_3$ or $Au(O_2CCF_3)_3$ as the source of gold.[19-21] These studies described preparation of complexes of bidentate *N,C* and tridentate *C,C,N* ligands, but not *N,C,N* examples. Most recently, Navares and co-workers showed that gold(III) complexes of N,C ligands could be prepared under normal conditions of reflux using a catalytic amount of a Rh(III) complex to effect the initial C–H activation.[22] We have now applied the same methodology to ligands related to those described above and have found that gold(III) complexes may be formed under these conditions (Fig. 8).[18]

Furthermore, we also showed that it is possible to make intermediate palladium(II) complexes of our *C,N,C* ligands (no toxic mercury) and that these, too, may be transmetallated to give the related gold(III) complex (Fig. 7).[18]

4. Conclusions

The studies described in this manuscript show how it possible to take a known luminophore and modify it chemically to confer liquid crystal properties. These liquid crystal properties were a function of: (i) the level of substitution on the pincer ligand, (ii) the level of substitution on the phenylacetylene co-ligand and (iii) the nature of the substitution on the phenylacetylene co-ligand. Certain of the modifications employed acted to enhance the solution

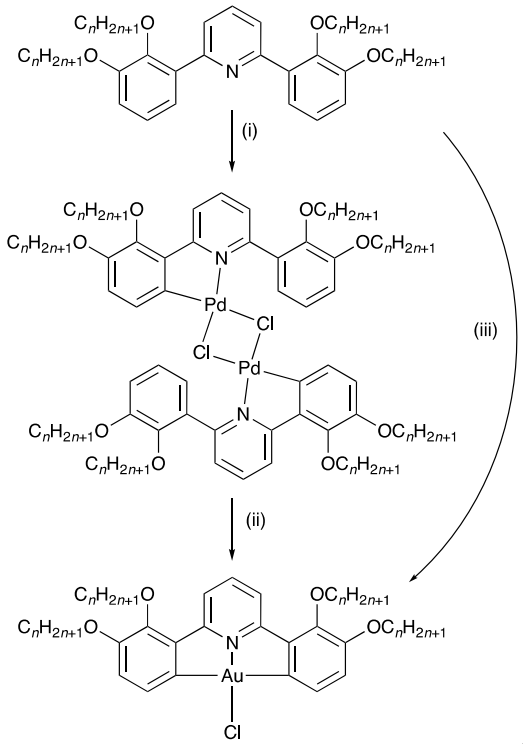


Figure 8 Mercury-free preparation of Au complexes: (i) $[PdCl_4]^{2-}$; (ii) $[AuCl_4]^-$; (iii) $[AuCl_4]^-$ (cat. $[Cp^*RhCl_2]_2$.

luminescence intensity of the complexes, but where devices were prepared, their emission efficiency (EQE) was not related to the solution emission efficiency (PLQY).

In addition, the synthetic studies that accompanied the work showed how related target complexes could be obtained without the use of mercury intermediates.

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6. Notes and References

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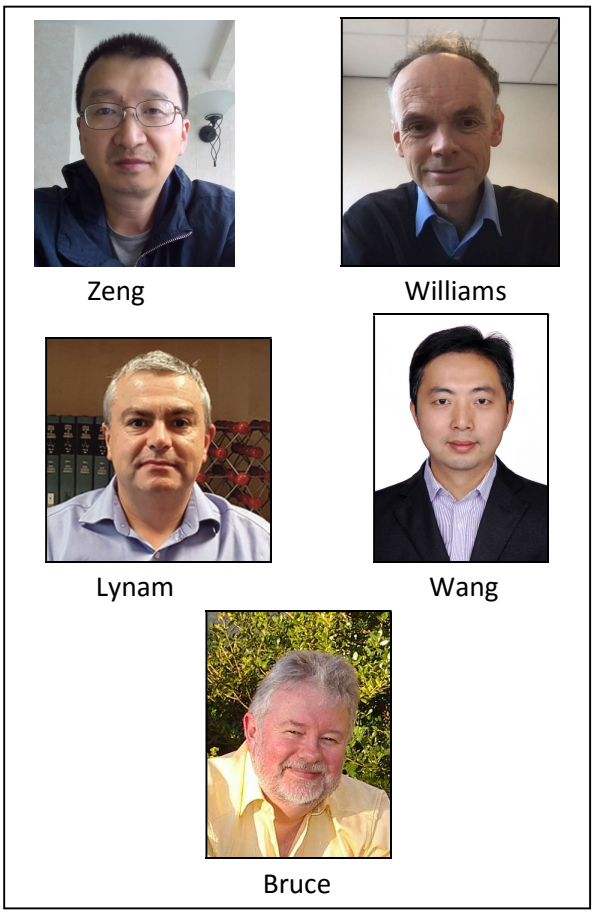
7. About the authors

The synthetic and liquid work reported was carried out at the University of York by Drs Rachel Parker and Alice McEllin (both PhD students at the time) under the guidance of Professors Duncan Bruce and Jason Lynam, and by Rachel Stracey as part of her final-year, undergraduate research project with Bruce. Single crystal structures were also solved in York by Drs Parker and Adrian Whitwood. Small-angle X-ray scattering on complex **11f**-10 was carried out by Dr Xiangbing Zeng from the University of Sheffield, while Professor Gareth Williams (Durham University) determined all of the solution photophysical data. Devices were fabricated by MSc students Denghui Liu, Xiankang Yu and Xinrui Chen at Changzhou University under the supervision of Professor Yafei Wang.



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