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**Luminescent Metallomesogens**

# Phosphorescent Mesomorphic Dyads Based on Tetraacetylethane Complexes of Iridium(III)**

*Anton M. Prokhorov, Amedeo Santoro, J. A. Gareth Williams, and Duncan W. Bruce**

*Dedicated to Professor Hubert Le Bozec on the occasion of his 60th birthday*

Complexes of iridium and platinum with aromatic ligands are of interest as emissive materials owing to their high spin–orbit coupling constants, which can promote phosphorescence from triplet states, a process that is otherwise formally forbidden. They are particularly relevant to organic light-emitting diode (OLED) technology, where the combination of charges leads to a surplus of triplet to singlet states, although their application in areas such as bioimaging[1] and sensing[2] have also received recent significant attention. Incorporation of emissive complexes can raise the maximum internal efficiency of an OLED to 100 % by promoting triplet emission.[3,4] Thompson and co-workers have shown that the bis(2-phenylpyridine)iridium(III) chromophore is a very effective triplet emitter, the physical properties of which make it suitable for incorporation into devices,[5] and the emission characteristics of which can be readily tuned through substitution of the ligands.[6]

To add the property of liquid crystallinity to emissive materials[7] is also of interest, for the ordered state of the molecules in the different mesophases suggests an improved pathway for the transport of charge carriers, whereas certain mesophases offer the possibility of polarized emission. We have reported liquid-crystalline Pt(II) phosphor compounds based on 1,3-di(2-pyridyl)benzene ligands that form columnar phases,[8] whereas those based on extended 2,5-diphenylpyridines show nematic and SmA phases with very high photoluminescent quantum yields.[9]

More recently and following a report of a luminescent, ionic, liquid-crystalline complex of Ir(III),[10] we reported the first example of a charge-neutral, luminescent, mesogenic complex of Ir(III) based on a hexacatenar phenylpyridine (ppy) ligand, with acetylacetonate (acac) as an ancillary ligand (**1a**).[11] In the same study, a related complex (**1b**) based on a tetracatenar ligand was found to be highly emissive ($\Phi = 50\,\%$) but not liquid-crystalline, whereas the di-μ-chloro dimer, **2**, of the same ligand was liquid-crystalline, but scarcely emissive ($\Phi < 1\,\%$; Figure 1).

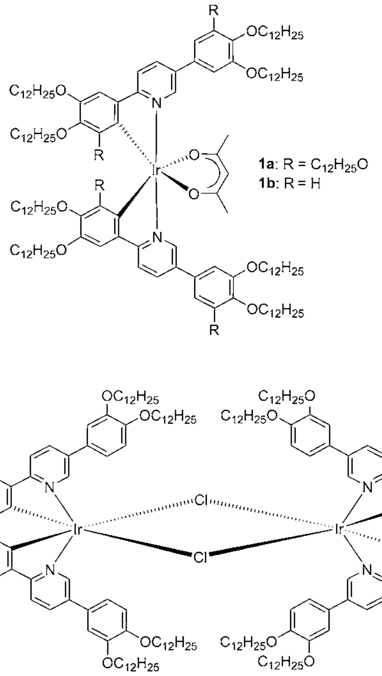

*Figure 1.* Examples of emissive Ir(III)acac monomer **1** and mesomorphic di-μ-chloro dimer **2**.

The results led to an assumption that the liquid crystallinity of **2** was somehow induced by the dichloro bridge which kept the two metal centers distant to create a molecular motif capable of self-organisation into a columnar phase. To test this idea and extend the system further, an article by Ma et al. was persuasive, in which 1,1,2,2-tetraacetylethane (tae) was used for the assembly of emissive Pt(II) dyads based mainly on substituted 2-phenylpyridines, for example, **3** (Figure 2).[12] It was, therefore, of interest to consider the tae ligand as a linker in dinuclear Ir(III) dyads based on polycatenar diphenylpyridines, to see if the increased separation of the two metal centers offered by tae compared to bridging Cl ligands can enhance the liquid crystallinity, while retaining the intense emission associated with monomeric complexes. The strategy also offers the possibility of exploring mesogenic heterodinuclear dyads: Ir(III)–Pt(II) complexes based on the

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[*] Dr. A. M. Prokhorov, Dr. A. Santoro, Prof. D. W. Bruce
Department of Chemistry, University of York
Heslington, York YO10 5DD (UK)
E-mail: duncan.bruce@york.ac.uk
Dr. J. A. G. Williams
Department of Chemistry, University of Durham
Durham DH1 3LE (UK)
Dr. A. M. Prokhorov
Department of Organic Chemistry, Ural Federal University
Mira 19, Ekaterinburg 620002 (Russia)

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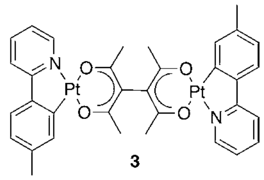

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*Figure 2.* Example of a Pt(II)tae complex.

tae ligand have scarcely been considered as emitters, with a single example in the patent literature.[13]

Thus, a series of dinuclear Ir(III) complexes was prepared based on ppy derivatives, with tae as the bridging ligand. The complexes, **5a**–**f**, were obtained from a set of 2,5-diphenylpyridines with different numbers of dodecyloxy chains, **4a**–**f** (Figure 3), by reaction with $IrCl_3 \cdot 3H_2O$ followed by cleavage of the resulting di-μ-chloro dimers with tae. The procedures used for the reactions were the same as for preparation of the monomeric acac analogues, except that a stoichiometric amount of tae was used to avoid the formation of a monocoordinated complex with the tae ligand.

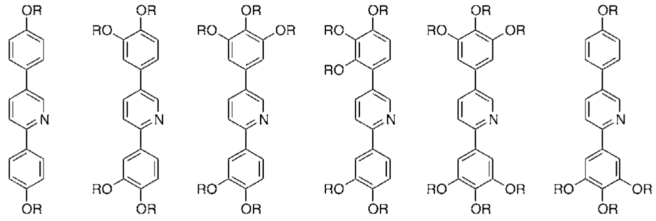
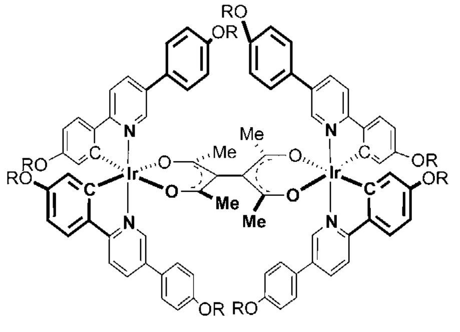


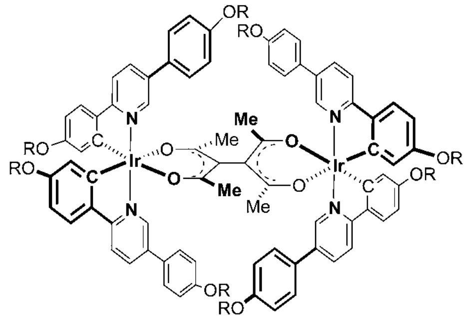
*Figure 3.* Set of polycatenar diphenylpyridine ligands, **4** ($R = C_{12}H_{25}$).

Being derived from bis(chelate) structures, the iridium centers are asymmetric and two asymmetric iridium centers assembled in one molecule can produce two diastereomeric forms: the *meso* form with ΛΔ-stereochemistry and the racemate of the ΔΔ- and ΛΛ-enantiomers with identical configurations at the metal (Figure 4).[14] In the case of di-μ-chloro dimers, only the racemic form is normally seen because of steric hindrance,[15] while for the tae dimers, the iridium centers are more distant and formation of both diastereomers is possible. Indeed, **5a**–**f** were formed as a mixture (shown by $^1$H NMR spectroscopy) of these two stereoisomers (Table 1) which, in some cases (**5a** and **5d**), could be separated by column chromatography, although it did not prove possible to identify which isomer was which.

All the dinuclear Ir(III) tae complexes synthesized are intensely luminescent in solution at room temperature. Thus, for **5a**, the emission is in the green-yellow region, $\lambda_{max} =$ 541 nm in $CH_2Cl_2$, while introduction of further alkoxy groups shifts the emission in the other five complexes to longer wavelengths, although there is little variation between them, all displaying orange luminescence with $\lambda_{max}$ between 578 and 588 nm (Table 1, Figure 5). In those cases where the racemate and *meso* forms could be separated from one another, they were found to have indistinguishable photophysical properties.



[{Ir(**4a**)$_2$}$_2$(tae)]
*meso* form (Λ,Λ)



[{Ir(**4a**)$_2$}$_2$(tae)]
racemate (Δ,Δ *or* Λ,Λ)

*Figure 4.* Structure of enantiomeric forms for complexes **5** with **5a** as exemplar.

*Table 1:* Thermal behavior and emission data of the Ir(III)tae complexes, **5**.

| [{Ir(**4**)$_2$}$_2$tae][a] | Transition and $T$ [°C] | Emission $\lambda_{max}$ [nm] (Quantum yield $\Phi$ [%])[b] |
|---|---|---|
| **5a** (isomer 1) | Cr 153 Iso | 541, 574 (58) |
| **5a** (isomer 2) | Cr 157 Iso | 541, 574 (58) |
| **5b** (2:1) | Cr 74 Col$_h$ 131 Iso | 586, 636 sh (55) |
| **5c** (2:1) | Cr 82 Iso | 587, 637 sh (45) |
| **5d** (isomer 1) | Cr 79 Col$_h$ 126 Iso | 588, 633 sh (43) |
| **5d** (isomer 2) | Cr 63 Col$_h$ 95 Iso | 588, 633 sh (43) |
| **5e** (4:3) | Cr 17 Col$_h$ 61 Iso | 582, 620 sh (38) |
| **5f** (4:3) | Cr 130 Col$_h$ 147 Iso | 578, 625 sh (50) |

[a] Unless stated, the samples are mixtures of diastereoisomers according to the ratios given in parentheses. [b] sh = shoulder.

The luminescence quantum yields, which are of the order of 50%, are rather high compared to typical Ir(III)acac complexes with simple ppy ligands,[16] and the luminescence lifetimes, which are around 4 μs in $CH_2Cl_2$ at 298 K, are slightly longer than those usually found for triplet-emitting [Ir(NC)$_2$(OO)] complexes emitting in this region (typically 1–2 μs).[17] Previously we noted elevated quantum yields and longer lifetimes for Pt(II) complexes of 2,5-diarylpyridines, compared to their parent and less substituted [Pt(ppy)(acac)] analogues.[6] The trend was interpreted in terms of the combined effects of reduced radiative and nonradiative decay rate constants, owing to the delocalization of the excited state over the aromatic ring at the 5-position of

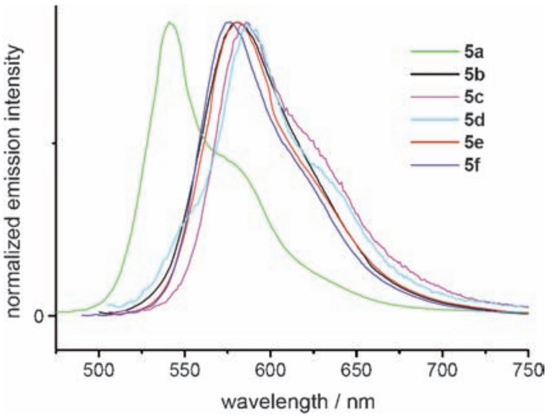


***Figure 5.*** Emission spectra of dinuclear complexes **5a–f** in $CH_2Cl_2$ at 298 K.

pyridine. This lowers the metal character in the excited state but also renders it less well-coupled to deactivating vibrational modes, such as those associated with the acac ligand.

In contrast to the monomeric acac analogues, which mostly are not liquid-crystalline, complexes **5b**, **5d**, **5e**, and **5f** are mesomorphic (Table 1), showing a columnar hexagonal mesophase. The phases were readily identified by their characteristic optical textures (Figure 6), best exemplified for the *meso* isomer of **5d**, where the very characteristic fern-like features are seen. Apparently, the bridging tae ligand optimizes the geometry of the molecule, making it more disc-like and inducing mesomorphism in the same way as the bridging chlorides in **2**. If separation of the racemate and *meso*-forms is possible, their transition temperatures are different and sharp melting and clearing points are observed. However, if a mixture is obtained, (**5b**, **5e**, **5f**) then both transitions are slightly broader, occuring over 1–2 °C at most. That **5a** is not mesomorphic is not surprising giving the low coverage of the dimer periphery by alkoxy chains and so it is with the tetracatenar ligand **4b** that mesomorphism is seen first. However, the mesomorphism is a delicate function of the number of chains as complex **5c** is not mesomorphic, while complex **5d** is, yet both are based on pentacatenar ligands. In comparing the transition temperatures as a function of ligand, it is generally apparent that more chains lead to lower clearing temperatures but, for example, comparison between **5b** and **5f** and between **5c** and **5d** shows that their mutual disposition is clearly important. Interestingly, the clearing points of the two isomers of **5d** are significantly different (by ca. 30 °C). Melting points are not compared as in most cases they refer to mixtures.

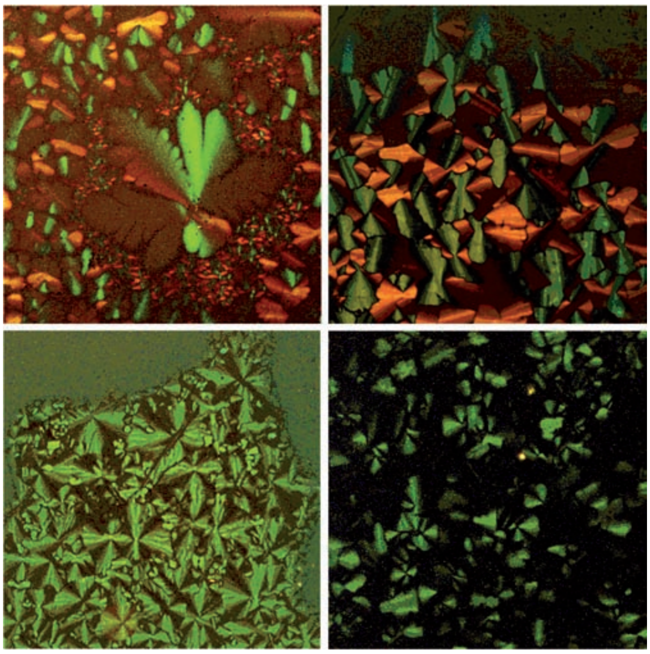


***Figure 6.*** Optical micrographs (on cooling) of the selected complexes: **5d**, isomer 1, 100 °C (top left), **5d**, isomer 2, 60 °C (top right), **5b**, mixture of diastereoisomers, 85 °C (bottom left), **5f**, mixture of diastereoisomers, 133 °C (bottom right).

Importantly, the iridium complexes also show luminescent behavior in the columnar mesophase, which is shown in Figure 7. The data show the relative luminescence intensity (measured at 590 nm, $\lambda_{ex} = 475$ nm) for complex **5b** as it is heated from the solid state, through its mesophase and into the isotropic liquid state. Note that we cannot rule out from these preliminary experiments that the abrupt decrease in intensity at $T_{Col\text{-}Iso}$ is due to the sample flowing out of the illuminating beam.

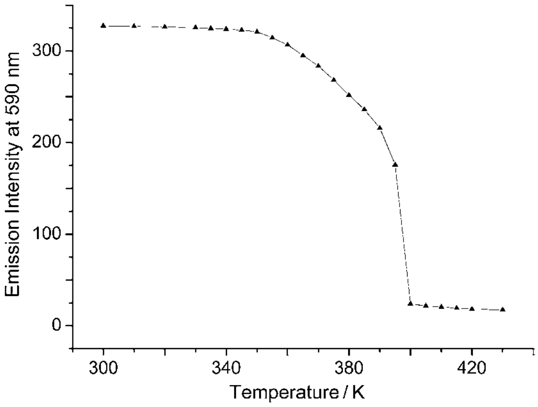


***Figure 7.*** Relative emission intensity of complex **5b** as a function of temperature.

The work has been extended towards heterodinuclear Ir(III)–Pt(II) complexes (**6**) of the same type. A complex with an iridium fragment $[Ir(\mathbf{4b})_2]$ and Pt(ppy) units connected by the tae ligand was prepared from $[Ir(\mathbf{4b})_2(\mu\text{-}Cl)]_2$ and the monomeric [Pt(ppy)(tae)] complex (Figure 8). This heterodimeric complex is not mesomorphic and simply melted to the isotropic state on heating. However, it exhibits intense emission ($\lambda_{max} = 588$ nm, $\Phi = 46\%$, $\tau = 4.9$ μs in $CH_2Cl_2$ at 298 K; Figure 8), similar to the homometallic Ir dimer of **4b**. Irrespective of the excitation wavelength, no significant Pt-based emission was observed at room temperature, which would be expected at around 485 nm (for the 0–0 band) based on the properties of [Pt(ppy)(acac)]. Clearly, under these conditions, energy transfer from the higher-energy Pt unit to

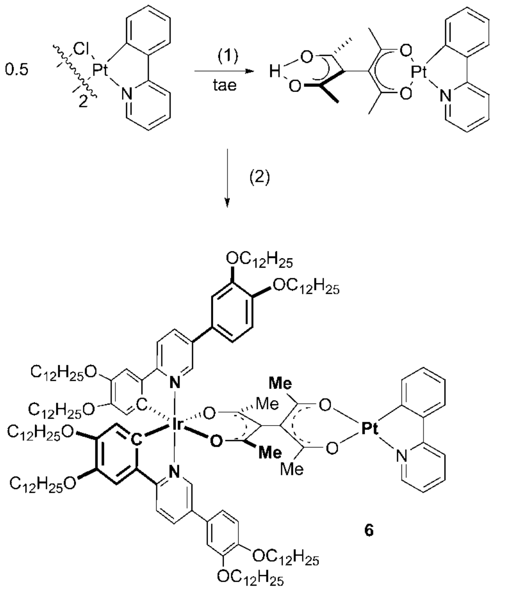


*Figure 8.* Heteronuclear Pt–Ir dyad, **6**. Reaction conditions: 1) $Na_2CO_3$, $CHCl_3$/EtOH, reflux; 2) [Ir(**4b**)$_2$(μ-Cl)]$_2$, $CHCl_3$/EtOH, $K_2CO_3$, reflux.

the lower-energy Ir moiety must be substantially faster than radiative decay of the Pt(ppy) unit. In contrast, in a frozen glass at 77 K, the main iridium-based band is accompanied by an additional set of weak bands that emerge at higher energy, the energies and profile of which are consistent with emission from the Pt unit (Figure 8). Apparently, under these conditions, the efficiency of energy transfer from the Pt to the Ir-based moieties is reduced. It is likely that the lowest-energy conformation of the system, predominantly adopted at low temperature, will be one that places the two planes of the tae unit essentially perpendicular to one another, inhibiting the conjugation between the metal centers. In related diplatinum heterodyads, energy transfer through the bridging tae ligand has been assigned to a Dexter-type mechanism.[9] The appearance of intense emission characteristic of the metal components in **6** contrasts with the behavior of a recently reported Pt–Ir dyad, in which the metals are connected by a phenyl-bridged diacac-type ligand.[18] In that case, only weak emission is observed, thought to originate from an excited state localized on the bridge. Meanwhile, a new $Pt_2Ir$ triad incorporating bis-NC-metallating phenylpyrimidine ligands has a high luminescence quantum yield, but the pertinent excited state is delocalized over the entire assembly, leading to the emission spectrum being distinctly different from that of the constituent units (Figure 9).[19]

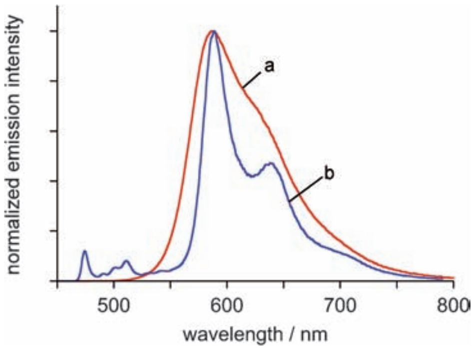


*Figure 9.* Emission spectra of the Pt–Ir dimer **6** a) in $CH_2Cl_2$ at 298 K and b) in a diethyl ether/isopentane/ethanol glass at 77 K; $\lambda_{ex} = 400$ nm.

In conclusion, this study shows how the use of tae-bridged metal centers can allow both liquid-crystalline properties and high triplet luminescence efficiences to be combined within a single molecule, opening up new potential in the design of light-emitting devices.

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