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Emissive Metallomesogens Based on 2-Phenylpyridine Complexes of Iridium(III)

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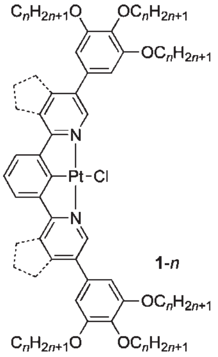
S *Supporting Information*

ABSTRACT: Preparation of Ir^{III} complexes using anisotropic 2,5-di(4-alkoxyphenyl)pyridine ligands leads to emissive, liquid-crystalline complexes containing bound Cl and dimethyl sulfoxide. Using analogous poly(alkoxy) ligands allows the preparation of bis(2-phenylpyridine)iridium(III) acac complexes, which are also mesomorphic. The observation of liquid crystallinity in octahedral complexes of this type is without precedent.

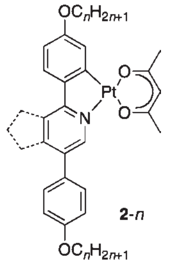
Light emission in organic light-emitting diode (OLED) devices arises from recombination of injected charges in a process analogous to the decay of an electronically excited state in a molecular system. The excited state arises when the electrodes inject an electron into the LUMO and a hole into the HOMO, which means that there are no spin constraints on the nature of that excited state. Statistically then, triplet states are formed with 3 times the probability of singlet states, which places an inherent limit of 25% on the efficiency of materials where spin constraints allow emission (recombination) only from the singlet state. However, in complexes of heavy transition elements, there is extensive spin−orbit coupling, which can modify the spin selection rules and allow intersystem crossing from the singlet to the triplet state and emission from the triplet manifold, increasing the theoretical efficiency of emission to 100%.[1]

With regard to desirable modifications of the components of OLED displays, the introduction of liquid crystallinity has certain attractions. Because liquid-crystal phases are ordered rather than amorphous, greater charge-carrier mobility can result, while if it is the emitting material that has liquid-crystal properties, then the emission can be polarized.

We recently described the preparation and photophysical properties of metallomesogens of Pt^{II}, which are emissive. Thus, we reported the modification of 1,3-bis(2-pyridyl)benzene ligands to give complexes (**1**-*n*) with columnar phases, where the emission wavelength could be controlled using the liquid-crystal mesophase.[2] We then described 2,5-di(4-alkoxyphenyl)pyridine complexes of Pt^{II}, (**2**-*n*), which showed nematic and smectic A phases and were very efficient emitters (Φ_{lum} = 57%).[3] Both of these systems are attractive, as previous studies have shown that the emission wavelength of the parent system may be tuned over a wide range of wavelengths.[4,5]



1-*n*



2-*n*

However, by far the most widely studied metal complexes for OLED applications are those based on the bis(2-phenylpyridine) iridium(III) chromophore. Tris(2-phenylpyridine)iridium(III) was first reported in 1985,[6] and since then, its derivatives have been studied widely[7] and have indeed been applied in commercial OLED displays following initial reports of their efficacy in device configurations.[8] As this is a well-studied material that has been used in commercial mixtures, the design and preparation of derivatives with liquid-crystalline properties is of great interest. However, this represents a not inconsiderable challenge, for while it is in general straightforward to realize liquid-crystalline materials from square-planar complexes such as those of Pt^{II}, it is an altogether different challenge with octahedral complexes.[9]

In considering how such materials can be designed, one must recognize the fact that the chromophoric unit is the bis(2-phenylpyridine)iridium(III) moiety, which means that liquid crystals must be realized *either* by modification of this ligand *or* by modification of the coligand(s), often an acetylacetonate, occupying the two remaining coordination sites. Previous work on octahedral metallomesogens has tended to show that in order to achieve an anisotropic complex, it is normally necessary *either* to have highly anisotropic ligands[10] *or* to use several highly substituted ligands[11] [see the examples in the Supporting Information (SI)]. However, Szerb et al.[12] recently reported

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Chart 1. Molecular Structure of Complex 3

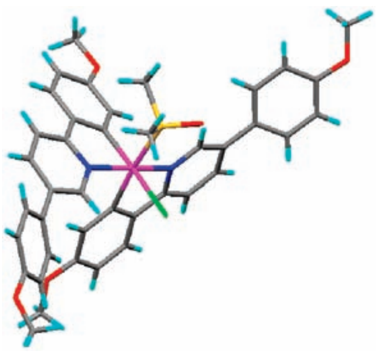
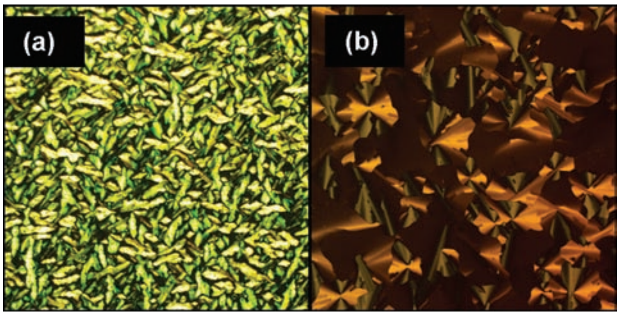
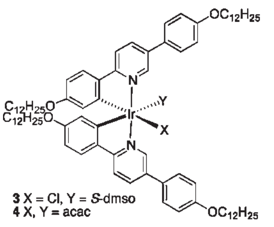


Chart 2. Optical Textures of Complexes (a) 5 (155 °C on Cooling) and (b) 7 (43 °C on Cooling)

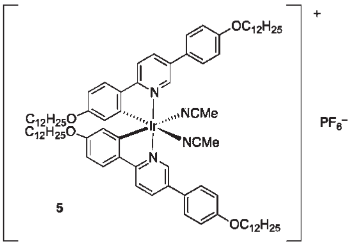


the mesomorphic, cationic iridium(III) complexes [Ir(ppy)$_2$(bipy′)][PF$_6$], wherein the liquid-crystal properties were driven by bipy′, a bis(3,4,5-trialkoxybenzoyl) ester of 4,4′-dihydroxymethyl-2,2′-bipyridine.

We therefore decided to commence an investigation using the 2,5-diphenylpyridine derivatives employed in the preparation of complexes **2**-*n*. Thus, we first prepared the di-μ-chlorodiiridium(III) dimer directly from the ligand and hydrated IrCl$_3$; the dimer was cleaved with dimethyl sulfoxide to give **3** and then reacted with Na$^+$acac$^-$ to give **4**.



3 X = Cl, Y = *S*-dmso
4 X, Y = acac



5

Complex **4** was emissive (λ_{em} = 540 nm; Φ_{lum} = 15%) but not liquid-crystalline, whereas, surprisingly, complex **3** showed both a lamellar and columnar rectangular phases. Complex **3** was also emissive (λ_{em} = 580 nm) but inefficiently so (Φ_{lum} = 0.5%). We were able to grow single crystals of an analogue of **3** with methoxy chains, for which X-ray diffraction (XRD) analysis gave the structure shown in Chart 1.[13] The complex crystallized in space group *Pbcn* along with some disordered CHCl$_3$ solvent molecules (omitted from Chart 1 for clarity) and showed the expected trans geometry of the two pyridyl nitrogens. The two Ir−N distances were identical at 2.070(3) Å, as were the two Ir−C bond lengths [Ir−C trans to Cl = 2.016(3) Å; Ir−C trans to *S* = 2.027(3) Å] when the estimated standard deviations are taken into account. Interestingly, the crystal structure of the analogous acac complex of unsubstituted 2,5-diphenylpyridine has been determined,[14] and no significant differences between the two structures were found.

Chart 3. Absorption Spectrum [at 298 K in CH$_2$Cl$_2$ (black line)] and Emission Spectra [at 298 K in CH$_2$Cl$_2$ (red line) and 77 K in EPA glass (blue line)] of Complex 5 Containing Dicatenar Ligands

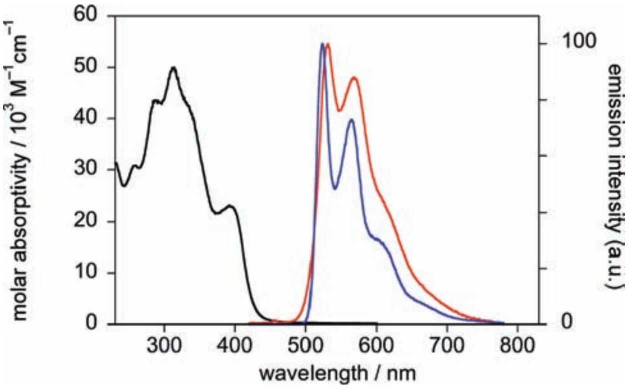
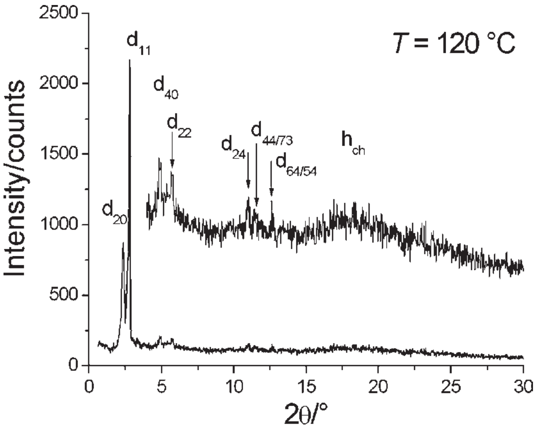


Chart 4. X-ray Diffraction Pattern for 3 at 120 °C



However, complex **3** is not stable over time, so cationic complex **5** was prepared by reaction of the di-μ-chloro dimer with AgPF$_6$ in MeCN.[15] This complex is stable and also liquid-crystalline, showing a columnar mesophase between 145 and 163 °C (the optical texture is shown in Chart 2a). The complex is photoluminescent in the green region of the spectrum (Chart 3; Φ_{lum} = 1.3% and τ = 1.75 μs in CH$_2$Cl$_2$ at 298 K).

In liquid-crystal terms, the fact that **3** is mesomorphic is remarkable, and there are no precedents in the literature for structures of this kind that form liquid-crystal mesophases. The higher-temperature mesophase of **3** is of a centered rectangular type (*c*2*mm*, *a* = 60.92 Å, *b* = 43.1 Å; indexed in Chart 4), which could be indicative of either a columnar rectangular phase or a

Chart 5. Polycatenar 2,5-Diphenylpyridine Ligands

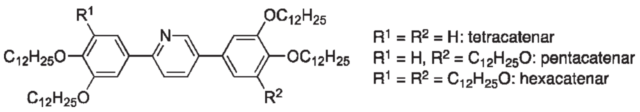
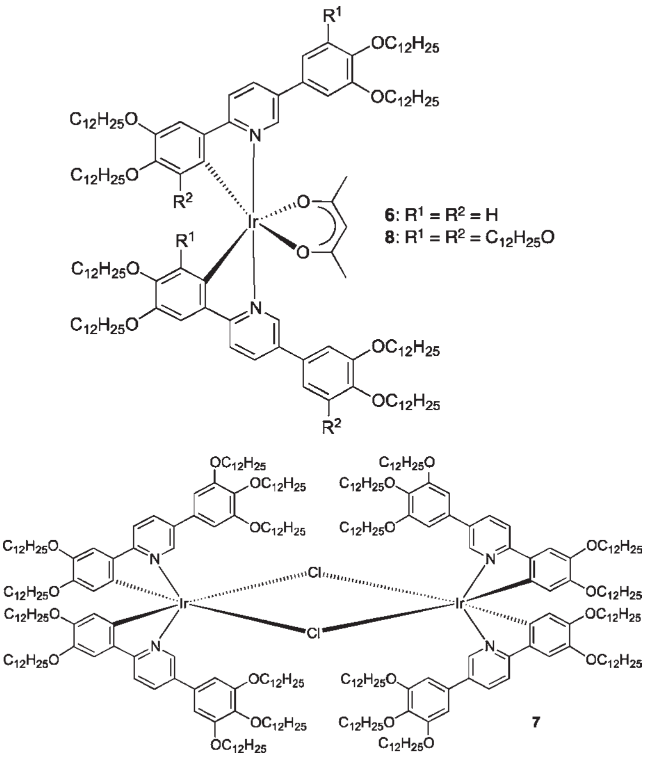


Chart 6. Structures of Complexes 6−8

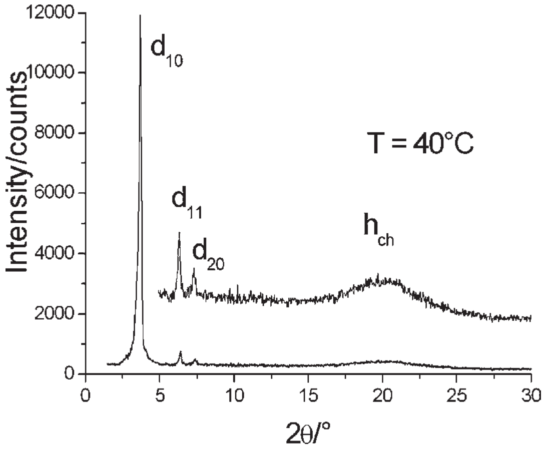


ribbon phase. In common with assignments recently made by us for mesomorphic complexes of platinum(III),[16] we prefer the ribbon phase, as the complexes are not those classically associated with the formation of columnar phases.

Despite the unprecedented mesomorphism found in **3** and **5**, the cationic nature of complex **5** would render it incompatible with conventional OLED architectures that require charge-neutral complexes, while the instability of **3** would also make it unsuitable. We therefore turned our attention to the induction of liquid-crystalline properties in neutral, inert, heteroleptic tris(chelate) complexes analogous to **4**.

Since the simple two-chain ligand used in complex **4** did not induce mesomorphism, polycatenar 2,5-diphenylpyridines containing four, five, or six terminal alkoxy chains were prepared (Chart 5).[17] Such an approach appeals to the design of highly substituted, mesomorphic tris(acac)metal(III) complexes, as mentioned above and reported in ref 11.

Chart 7. X-ray Diffraction Pattern of Complex 7



Using these ligands produced some very interesting results in that we were eventually able to demonstrate liquid-crystal properties not only in a monomeric complex with acac as the coligand but also in the precursor di-μ-chloro dimers. Thus, use of the tetracatenar ligand led (via the di-μ-chloro dimer) to complex **6**, which, while not a liquid crystal, was a very bright orange emitter (λ_{max} = 586 nm, Φ_{lum} = 50%, τ = 5.2 μs). However, the reaction of a pentacatenar 2-phenylpyridine with hydrated $IrCl_3$ led to dimer **7** (Chart 6), which showed a columnar hexagonal liquid-crystal phase from room temperature (where it already existed in the mesophase) to 75 °C, at which temperature it cleared. The optical texture is shown in Chart 2b and the XRD pattern in Chart 7 (a = 27.72 Å). Unusually for such a chloro-bridged dimer, **7** is photoluminescent, albeit rather weakly so (λ_{max} = 570 nm, Φ_{lum} = 0.8%, τ = 5.1 μs; see the spectra in the SI).

Cleavage of this dimer to give the corresponding acac monomer led to a glassy complex with no liquid-crystal properties, as had been observed for the dicatenar analogue **4**. Conversely, use of a hexacatenar 2-phenylpyridine gave a di-μ-chloro dimer that was not liquid-crystalline, but in this case its corresponding monomeric acac complex (**8**) was, and a columnar hexagonal liquid-crystal phase was observed between 31 and 66 °C (texture in Chart 3b, XRD pattern in the SI; a = 27.54 Å). This complex was quite strongly luminescent in the orange region of the spectrum (λ_{max} = 582 nm, Φ_{lum} = 9.1%). Clearly then, the observation of liquid crystallinity is a fine balance relating to the number and disposition of terminal alkoxy chains on the 2-phenylpyridine ligand, as is the efficiency of emission, control of which requires more detailed investigation. Nonetheless, use of these ligands has led to liquid-crystalline analogues of highly desirable luminescent iridium(III) complexes with mesophases just above room temperature, offering an exciting prospect for future development.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data (CIF), structure and preparation of ligands, further photophysical data, and selected optical spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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