Metallomesogens

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Phosphorescent, Terdentate, Liquid-Crystalline Complexes of Platinum(II): Stimulus-Dependent Emission**

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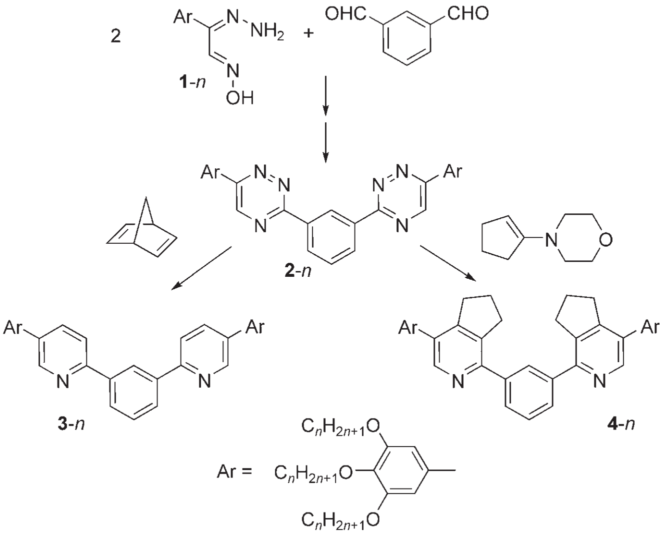
In memory of Naomi Hoshino-Miyajima

In addition to their widespread use in electro-optic displays, liquid crystals have huge potential for application in a range of scientific and technological areas.[1] For example, in molecular electronics, their ability to self-organize spontaneously into well-defined structures gives improved morphologies, high charge-carrier mobilities, and orientation-dependent effects such as polarized emission. Luminescent liquid crystals have the potential for use in organic light-emitting diodes (OLEDs). Although early examples were based on purely organic materials,[2] in recent years, luminescent metallomesogens have been reported.[3]

Indeed, phosphorescent metal complexes, in particular bis(N,C)-coordinated Ir^{III}[4] and N,C,N-coordinated Pt^{II},[5] are the best performing emitters for use in OLEDs[6,7] and the incorporation of these luminophores into liquid-crystal systems is of interest. The square-planar geometry of Pt^{II} makes it easier than Ir^{III} to adapt for liquid-crystal design. Thus, Venkatesan et al. reported columnar mesophases from suitably substituted Pt^{II} complexes of 2-phenyl- and 2-thienylpyridines, where the disc-like motif was generated primarily through the use of hexacatenar β-diketonates.[8] Damm et al.[9] and Ghedini et al.[10] have also reported luminescent complexes of platinum(II) and palladium(II), respectively, based on orthometallated ligands, while Camerel et al.[11] and Cardolaccia et al.[12] reported luminescent, gel-forming Pt^{II} complexes of terpyridines and alkynes, respectively.

Our attention was caught by the terdentate N,C,N-coordinated Pt^{II} complexes of 1,3-dipyridylbenzenes for which Williams and co-workers recently reported exceptionally high quantum efficiencies.[13] Herein, we describe a new synthetic route to functionalized 1,3-di(2-pyridyl)benzenes that does not use cross-coupling methodologies and which allows ready access to materials disubstituted in the pyridine 5-positions. The synthesis is applied to the design of complexes that represent the first examples of liquid crystals based on this excellent Pt^{II} luminophore.

The methodology is adapted from one developed earlier for the synthesis of pyridines[14] and, in particular, of 2,2′:6′,2″-terpyridines.[15] Recently, we described the use of this methodology in the preparation of mesomorphic phenyltriazines and phenylpyridines[16] as well as inherently mesomorphic terpyridines.[17] The design strategy adopted herein required the preparation of hexacatenar systems with half-disc geometries by functionalization of the 5-positions in pyridine rings with 3,4,5-trialkoxyphenyl fragments. Thus, the ligands were prepared[14] by condensing the hydrozone oxime precursor (**1**-1) with isophthalylaldehyde to give the di-*N*-oxide of triazine **2**-1 (Scheme 1). This was reduced to the triazine itself before being converted into precursors **3**-1 and **4**-1 in a retro Diels–Alder reaction using either 2,5-norbornadiene or 1-morpholinocyclopentene, respectively. Long alkyl chains were then introduced by demethylation followed by O-alkylation. The final complexes (**5** and **6**, Figure 1) were then obtained by reacting the finished ligands with $K_2[PtCl_4]$ in AcOH.



Scheme 1. Synthesis of ligands **3**-*n* and **4**-*n*, where *n* is the carbon chain length of the alkyl substituents on Ar.

The ligands themselves were not liquid-crystalline and melted directly to the isotropic fluid between 30 and 80 °C.

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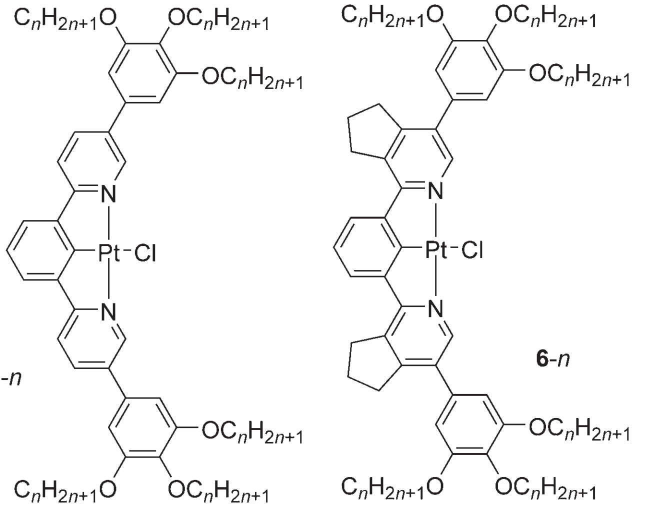

5-*n*

6-*n*

Figure 1. Structure of the new, phosphorescent platinum(II) complexes **5**-*n* and **6**-*n*.

Table 1: Thermal behavior for the new platinum(II) complexes.

Compound	Transition[a]	T [°C]	ΔH [kJ mol^{-1}]	ΔS [J K^{-1} mol^{-1}]
5-4	Cr–Iso	254	–	–
5-6	Cr–Col$_\text{r}$	126	2.4	6
	Col$_\text{r}$–Iso	187	9.1	20
5-8	Cr–Col$_\text{r}$	149	1.9	5
	Col$_\text{r}$–Iso	167	9.2	21
5-10	Cr–Cr′	80	9.2	26
	Cr′–Col$_\text{r}$	91	3.0	8
	Col$_\text{r}$–Iso	151	16.6	39
5-12	Cr–Cr′	81	21.5	61
	Cr′–Col$_\text{r}$	92	3.8	10
	Col$_\text{r}$–Iso	151	16.6	39
6-10	Col$_\text{h}$′–Col$_\text{h}$	145	5.9	14
	Col$_\text{h}$–Iso	220	12.3	25
6-12	Cr–Col$_\text{h}$′	33	7.8	26
	Col$_\text{h}$′–Col$_\text{h}$	143	5.0	12
	Col$_\text{h}$–Iso	206	9.2	19

[a] The abbreviations are explained in the text.

However, coordination to Pt$^{\text{II}}$ induced mesomorphism, summarized in Table 1. Thus for complexes **5**-*n*, the shortest-chain homologue (**5**-4) simply melted to the isotropic state (Iso) at 254 °C and no monotropic phases were seen on cooling. All of the other homologues, with peripheral chains from hexyloxy to dodecyloxy showed a columnar phase with a range of up to 61 °C. For complexes **6**-*n* containing cyclopentene rings, two mesomorphic homologues are reported, **6**-10 and **6**-12. The optical textures (see Supporting Information) confirmed that the mesophases were columnar. Comparison of the transition temperatures between the two series shows that longer chains are required in series **6**-*n* before mesomorphism is observed and that both the crystal (Cr) and liquid-crystal phases are stabilized strongly by the introduction of the cyclopentene group.

The mesophase symmetry for two derivatives, **5**-10 and **6**-10, was examined by X-ray diffraction (Figure 2). The data (see Supporting Information) show clearly that, in **5**-10, the phase is rectangular (Col$_\text{r}$), belonging to plane group *c2mm* with $a = 59.08$ and $b = 38.25$ Å. Three, broad, wide-angle reflections at 3.4, 4.3, and 4.7 Å are assigned to aromatic–aromatic separation, Pt···Pt separation, and alkyl chain separation, respectively. If unit density is assumed, then it can further be calculated that a columnar slice of 4.3 Å thickness with a ring–ring separation of 3.4 Å contains approximately two molecules with antiparallel arrangement, also consistent with the proposed Pt–Pt separation (see Supporting Information). Contact preparations between **5**-10 and other homologues confirm Col$_\text{r}$ symmetry throughout the series (in the process of contact preparation, two samples are brought together in their liquid crystal phase where the phase identity for one sample is known. If the two are co-miscible, then the phase of the second material is identified. If they are not, then no information is obtained).

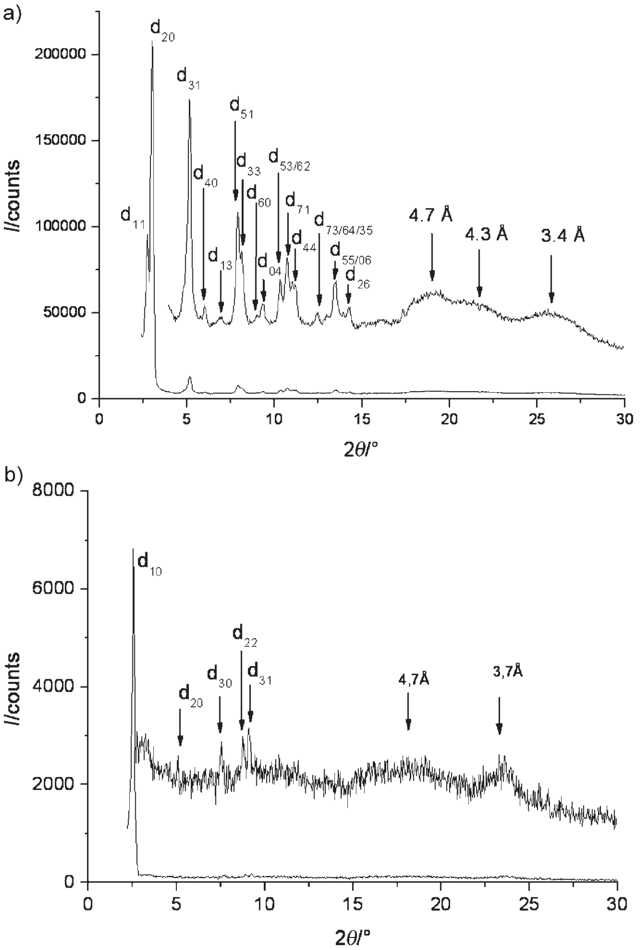

Figure 2. X-Ray diffraction pattern for a) **5**-10 at 120 °C and b) **6**-10 at 180 °C.

Complex **6**-10 however clearly shows hexagonal symmetry (Col$_\text{h}$, $a = 43.44$ Å). In this case, a $d(001)$ reflection is seen at 3.7 Å, a result of the greater steric demands of the fused cyclopentene ring, whereas $d_{\text{Pt-Pt}}$ and the molten alkyl chains give rise to a broad reflection in the approximate range $17° < 2\theta < 20°$. The breadth of the wide-angle reflection makes structural predictions more difficult, but the data show that at unit density, between two and three molecules are contained within a slice of column between 3.3 and 5 Å thick. The lower-temperature phase, assigned as $\mathrm{Col_h}'$, shows the same reflections as the $\mathrm{Col_h}$ phase plus others that may be indexed into plane group *p6mm*. Consistent with theory, the two phases of the same symmetry are separated by a first-order phase transition; the lattice parameter a increases to > 46 Å at the transition. For **6**-12, a melting point is observed on the first heating scan, but cooling back to ambient temperature leads to a glassy phase. Indeed, **6**-10 does not show a melting point and the material is obtained from solution in the $\mathrm{Col_h}'$ phase.

Complexes **5**-*n* and **6**-*n* are luminescent at room temperature in dichloromethane solution and the emission spectra (see Supporting Information) are reminiscent of those reported for the parent complex.[11] However, the component bands appear to be broader and quantum efficiencies lower ($\phi = 0.07$), probably the result of more efficient non-emissive vibronic deactivation. Compared to **5**-*n*, complexes **6**-*n* (with the cyclopentene rings) show absorption and emission spectra that are shifted hypsochromically, and emission quantum yields that are generally greater ($\phi = 0.12$). This effect arises because the steric effect of the cyclopentene rings does not allow such efficient overlap of the pyridine rings with the outer aromatic rings, raising the energy of the HOMO–LUMO gap. Furthermore, the steric crowding (evident in a related X-ray structure[17]) will reduce motional freedom and hence vibronic deactivation.

In the present system, it has been observed that the same sample of pure **5**-6 can produce different emission colors depending on the method of sample preparation—that is, the thermal history. Thus, Figure 3 a shows a photomicrograph of the columnar mesophase of **5**-6 in a glassy state. Large, well-developed domains are seen obtained by cooling slowly from the isotropic melt to 170 °C and then rapidly to room temperature. The emission spectrum (Figure 3 a,bottom) reveals structured monomer emission at 575 nm and 624 nm (Figure 3 a,inset shows the luminescence color). Figure 3 b however shows the photomicrograph obtained when the same complex was cooled rapidly directly from the isotropic melt. Here the domains are very small, which means that there is a high concentration of (isotropic) grain boundaries; no monomer emission is observed, rather excimer-like emission (660 nm; Figure 3 b,inset shows the luminescence color). The two different samples were investigated using X-ray diffraction, although in these experiments it was not possible exactly to reproduce the rate of cooling in the purely optical experiments. No difference was observed, but in fact all that might have been expected would be a sharpening of the *d*(10) and *d*(001) reflections to indicate different correlation lengths. However, while by optical microscopy the observed domains are small in the sample with the longer-wavelength luminescence (Figure 3 b), they are still large on a molecular length scale and so even if we were to reproduce the experiment precisely, it is unlikely that any difference would be observed between the two samples represented in Figure 3.

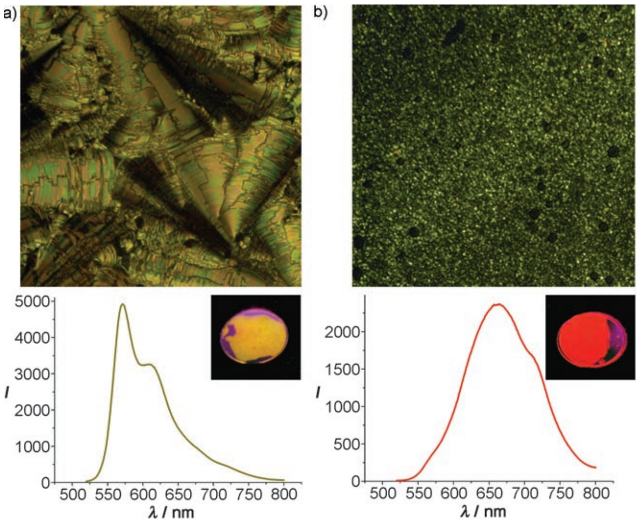

Figure 3. **5**-6 at room temperature, Top: Photomicrographs (taken between crossed polarisers), Bottom: emission spectra ($\lambda_{\text{excitation}} = 420$ nm.), Inset:real samples of pure films sandwiched between glass slides; a) fast cooled from the LC phase after the texture is fully developed, b) fast cooled direct from the isotropic phase.

The photophysical properties of $\mathrm{Pt^{II}}$ complexes are known to be very sensitive to intermolecular association,[18] in solution as well as in the crystalline state. The former relate to dynamic processes while the latter are highly dependent on the overall organization in the crystal lattice. Liquid crystals present something of an intermediate situation, with molecules organised dynamically into different mesophases. Thus, in the columnar phase (Figure 3 a), complexes are constrained into an antiparallel arrangement in which they behave independently (as monomers). However, in Figure 3 b the sample is dominated by isotropic grain boundaries in which the complexes are free to adopt excimer-like[*] structures from which emission is observed.

Attention then turned to the production of thin films by spin coating, where it was found that a pure film of **6**-10 displayed only excimer-like emission ($\lambda = 660$ nm; excitation spectra in Supporting Information). However, after heating the film to 110 °C followed by cooling to room temperature, there was a drastic change in emission color from the red of the excimer to yellow, indicating simultaneous emission from monomer and excimer (Figure 4). However, if the film is subjected to mechanical disturbance (such as rubbing), the red emission of the excimer returns. A further heat–cool cycle re-establishes monomer emission. Thus, emission is under tribological control and the initial state can readily be re-set, suggesting re-usable, stimulus-responsive applications.

In summary, preparation of liquid-crystalline derivatives of a highly efficient N,C,N-$\mathrm{Pt^{II}}$ luminophore has been realized. Furthermore, it is found that emission in the liquid-crystal phase is characteristic of the monomeric complex, very different from the excimer-like emission that normally characterizes non-liquid-crystalline analogues.[7] However, it is also shown that the emission of pure films is responsive both to method of preparation and tribological stimulation, so that it is possible to move controllably between monomer- and excimer-like states.

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[*] Strictly, the term “excimer” applies only in solution. It is used here to imply an excited dimer formed in a condensed phase.

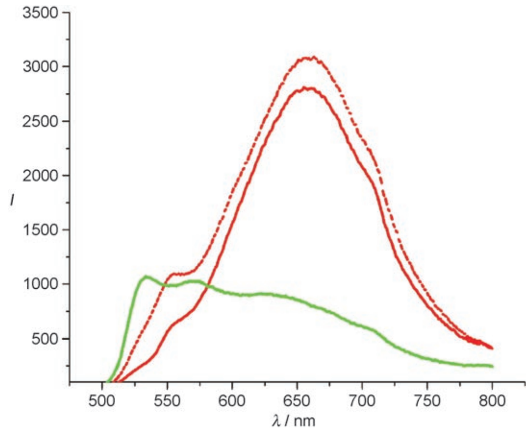

Figure 4. The emission spectra of pure films of **6**-10 obtained by spin-coating the 10 mg cm^{-3} solution on a glass surface, as prepared (red), the same slide but after heating to 110 °C for 5 min (green), the same slide, disrupted mechanically at room temperature (dotted red). $\lambda_{\text{excitation}} = 410$ nm.

Experimental Section

All experimental data are found in the accompanying Supporting Information.

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