

Generation of metallomesogens using common ligands functionalised with liquid-crystalline moieties†‡

Indudhara S. Shashikala and Duncan W. Bruce*

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Functionalisation of 2,2'-bipyridine or acetylacetone with an alkyleneoxycyanobiphenyl group induces liquid-crystalline properties in simple metal complexes.

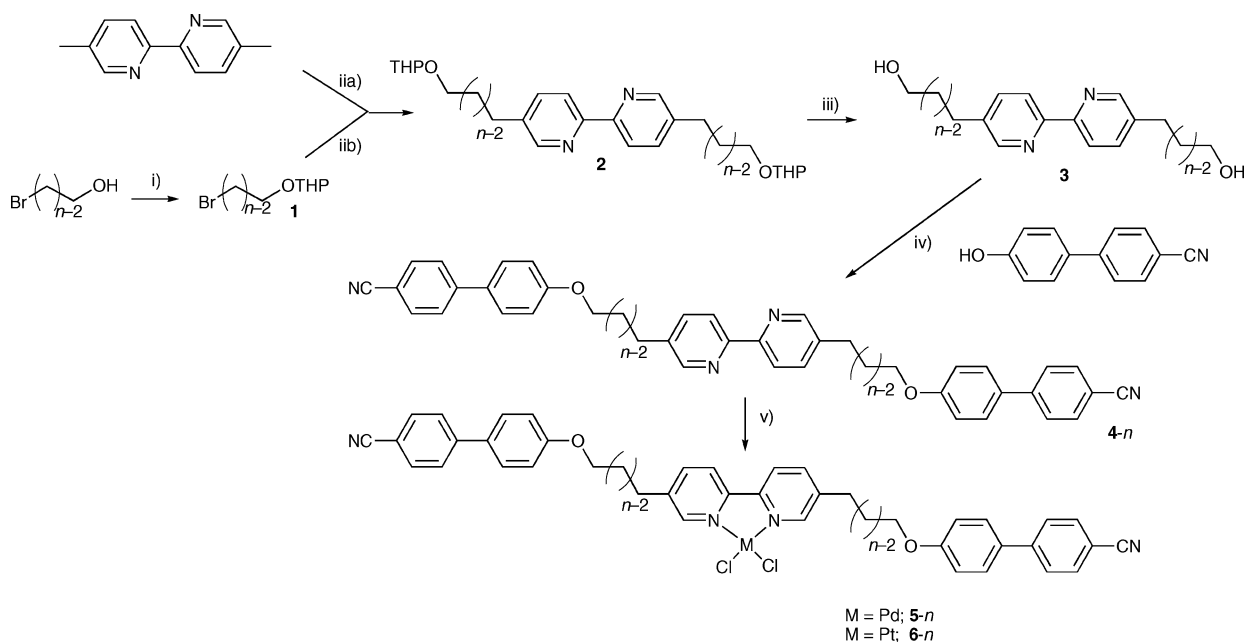
The synthesis and study of metallomesogens has been a very active area of research for more than twenty years and different approaches have been adopted in order to accommodate different metal centres.¹ For example, in many discotic systems the situation is reasonably straightforward and it has been sufficient to take a planar metal–ligand combination and ‘decorate’ the periphery with six to eight alkyl chains to generate a complex that will stack to form a columnar mesophase. Examples include, for example, β -diketonato complexes of copper(II), metallophthalocyanines and, more exotically, tetrapalladium(II) macrocycles.¹

With rod-like (calamitic) mesogens, the situation has always been a little more delicate and a slightly more careful choice of metal–ligand combination has been required. For example, from our own work we know that liquid-crystalline cyanobiphenyls (really just elaborated benzonitriles) will generate metallomeso-

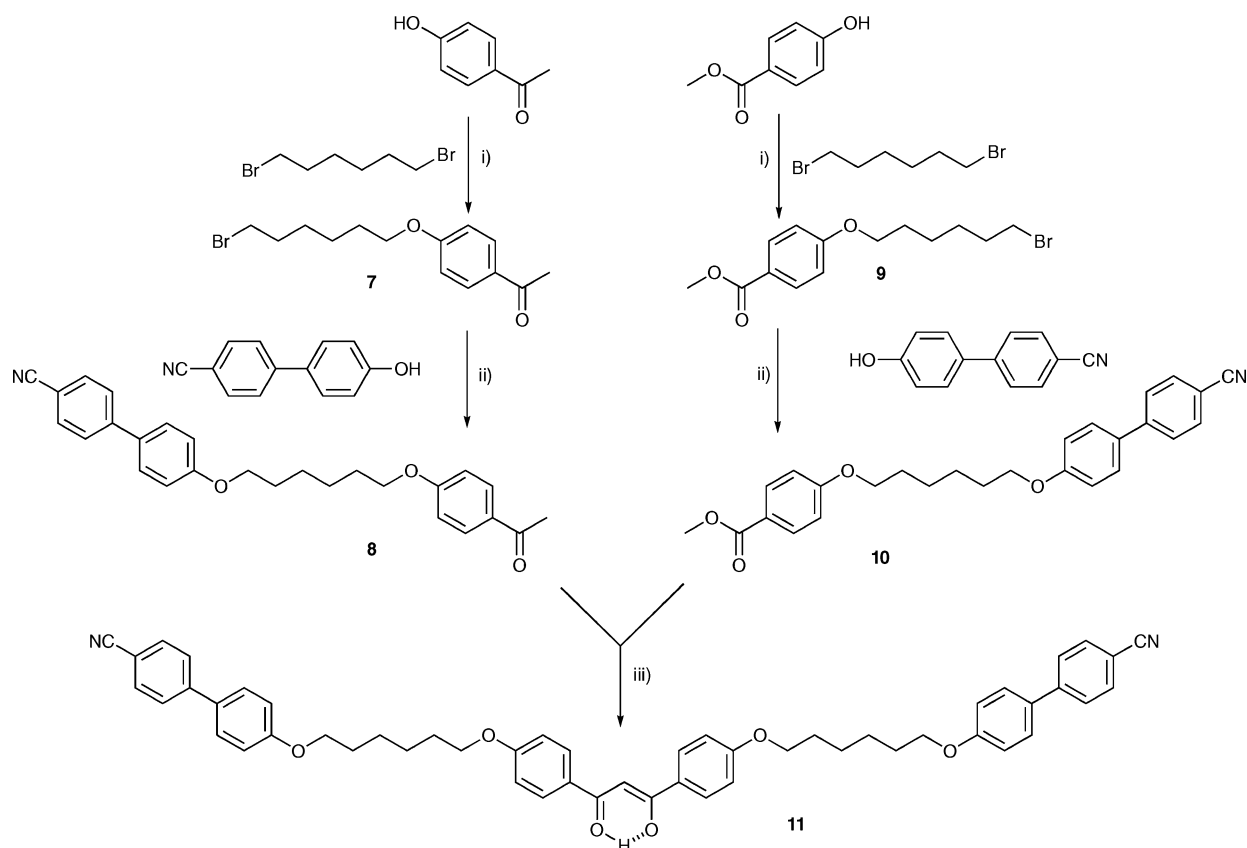
gens when complexed to palladium(II) and platinum(II),² but are poor ligands to rhodium(I) and silver(I). On the other hand, 4-alkoxystilbazoles³ (elaborated pyridines) are not ideal ligands for generating metallomesogens when bound to MCl_2 ($M = Pd, Pt$), yet they do lead to metallomesogens with Rh^I , Ir^I and, especially, Ag^I .⁴ In contrast, di- and tri-alkoxystilbazoles are good ligands for Pd^{II} , Pt^{II} and Ag^I , but not Rh^I and Ir^I . Thus, there is a sense in which ligands are tailor-made for particular complexes (this is also true in discotic systems) and while this a valid approach to their study, there is perhaps a need for more generic ligands.

With this in mind, we identified two common and widely used ligands, namely bipyridine and acetylacetone, and elected to elaborate each with a cyanobiphenyl, which would be bound to the core ligand *via* a flexible alkyl spacer. There is a sense in which a similar approach has been adopted previously, where Cardinaels *et al.*⁵ described the preparation of extensively derivatised 1,10-phenanthrolines (imidazo[4,5-*f*]-1,10-phenanthrolines, which were then bound to three alkyleneoxycyanobiphenyls through a phenyl ring). Indeed, the literature shows⁶ that almost any chemical core can be made liquid crystalline if sufficient mesogenic moieties are attached to it. However, the work described here offers, we believe, a simpler and more generally applicable approach.

The bipyridine ligands were synthesised as described in Scheme 1. Thus, the hydroxyl function of 1-bromo-11-hydroxyundecane was protected with THP to give **1**, which was then



Scheme 1 Synthesis of the mesomorphic bipyridines and their Pd and Pt complexes: (i) 3,4-dihydro-2H-pyran, CH_2Cl_2 ; (iia) LDA, *n*-BuLi, THF, $-70^\circ C$; (iib) **1**, $-30^\circ C$; (iii) *p*-TSA, EtOH, reflux; (iv) DEAD, CH_2Cl_2 , $0^\circ C$; (v) $[PdCl_2(NCPh)_2]$, $CHCl_3$ or $K_2[PtCl_4]$, HCl, EtOH.



Scheme 2 Preparation of the new β -diketonates: (i) NaHCO_3 , KI, acetone; (ii) K_2CO_3 , DMF, 80 °C; (iii) NaH, DME.

reacted with the dianion of 5,5'-dimethyl-2,2'-bipyridine (*via* reaction with LDA) at low temperature to give the coupled product, **2**. Deprotection of the alcohol led to **3** which was then coupled with 4-hydroxy-4'-cyanobiphenyl under Mitsunobu conditions to give bipyridine **4**. Bipyridine **4–12** was mesomorphic and melted at 130.2 °C to give a nematic phase that persisted to 149.1 °C when it cleared. Bipyridine **4–8**, with the shorter methylene linking group was, however, not mesomorphic and simply melted directly to the isotropic state at 214 °C. The analogous ligand was also prepared using 4,4'-dimethyl-2,2'-bipyridine and with $n = 12$, but it was not mesomorphic, melting directly to the isotropic liquid at 139 °C. The related palladium complex was similarly devoid of mesomorphism.

Considering other common ligand systems, we next turned our attention to β -diketonates. β -Diketonate ligands have been used extensively in metallomesogen chemistry,¹ and in many complexes, mesomorphism arises from complexation to diphenyl β -diketonates functionalised with between two and six alkoxy chains. Most extensively studied have been 2 : 1 complexes with Cu^{II} , Pd^{II} and $\text{O}=\text{V}^{\text{IV}}$, although 1 : 1 complexes are known with Tl^{I} and Ir^{I} , 3 : 1 complexes with ions such as Co^{III} and Mn^{III} and there is even a 4 : 1 complex with Zr^{IV} . In addition, β -diketonates are co-ligands in a range of complexes, mostly with Pd^{II} or Pt^{II} bound to some *ortho*-metallated such as a Schiff base or a phenylpyridine. In many of these cases, acac itself is used as a simple 'spectator' co-ligand, but in other cases, more highly functionalised diketonates are employed, which modify the properties of the parent complex.

Cyanobiphenyl-functionalised derivatives were prepared as shown in scheme 2. Thus, excess of 1,6-dibromohexane was reacted with 4-hydroxyacetophenone to give the bromoalkyl-functionalised acetophenone (**7**) which, upon reaction with 4'-hydroxy-4-cyanobiphenyl, gave intermediate acetophenone **8**. A similar pathway gave the intermediate methyl benzoate **10** *via* a bromoalkyl-functionalised methyl benzoate (**9**). Claisen condensation of **8** and **10** then led to the target β -diketonate, **11**.

Examination of the thermal properties of **11** and some of its intermediates showed that acetophenone **8** was mesomorphic, melting to give a nematic phase at 99.4 °C, which cleared to isotropic liquid at 122.4 °C. Similarly, the methyl benzoate **10** showed a nematic phase with transition temperatures rather similar to those of **8** (Table 1). Considering the complete ligand, **11**, heating caused the compound to melt at 152.5 °C to give a nematic phase, which persisted to 201.1 °C when clearing was observed.

Bipyridines **4** were reacted with $[\text{PdCl}_2(\text{NCPh})_2]$ in acetone or with PtCl_2 in the melt,⁷ to give $[\text{PdCl}_2(\text{4})]$ (**5–n**) and $[\text{PtCl}_2(\text{4})]$ (**6–n**), respectively, which were characterised by NMR spectroscopy and by elemental analysis (details in ESI†). Complex **5–12** shows a monotropic SmA phase, so that on heating, it melted directly to the isotropic state at 179.1 °C and on cooling, the SmA phase was seen to grow in at 156.5 °C, persisting until the complex crystallised, normally around 110 °C. Interestingly, **5–12** was found to be soluble in 4'-pentyl-4-cyanoterphenyl (T15) at 128 °C at a concentration of 10%. Complex **6–12** was similarly

Table 1 Thermal properties of the new liquid crystals

Compound	Transition ^a	<i>T</i> /°C	ΔH /kJ mol ⁻¹
4–12	Cr–N	130.2	72.3
	N–I	149.1	6.3
5–12	Cr–I	179.1	54.0
	(SmA–I)	(156.5)	(5.7)
6–12	Cr–I	176.5	52.3
	(SmA–I)	(150.3)	(2.4)
8	Cr–N	99.4	45.4
	N–I	122.4	3.3
10	Cr–N	125.9	31.8
	N–I	137.4	4.9
11	Cr–N	152.5	70.5
	N–I	201.1	7.7
12	Cr–N	224.6	46.1
	N–I	241.3	6.6
13^b	Cr–SmA	130.0	—
	SmA–N	176.0	—
	N–I	240.0	—
15	Cr–I	202.0	43.8
	(N–I)	(168.0)	(2.6)
	(SmA–N)	(136.0)	(1.9)

^a Reporting monotropic transitions in this way indicates that temperatures were obtained on re-heating from the lower phase and as such are thermodynamic temperatures. ^b Transition temperatures from microscopy. DSC data not available, see text.

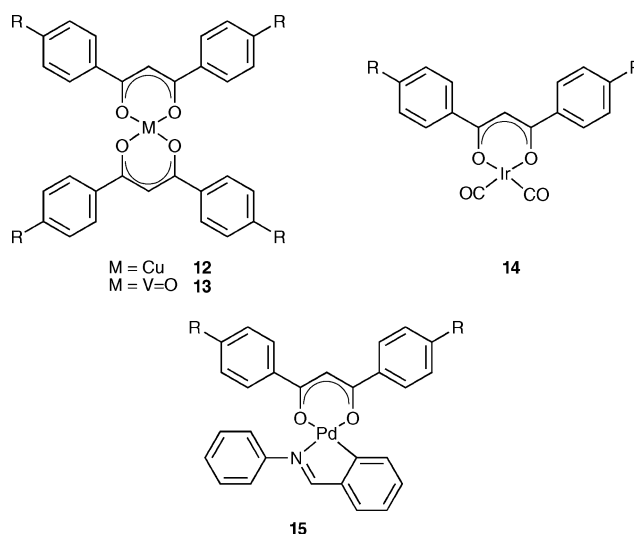
mesomorphic, melting at 176.5 °C and forming a monotropic SmA phase at 150.3 °C.

Mesomorphic complexes of MCl₂ in combination with bipy-based ligands are rare. Complexes formed from 5,5'-disubstituted-2,2'-bipyridines did not show liquid crystal properties, while more recently, Pucci *et al.*⁸ reported some dichloro-palladium and -platinum complexes of alkyl esters of 2,2'-bipyridine-4,4'-dicarboxylic acid which were luminescent and which showed an ill-defined lamellar phase.

Complexes were also made by reacting **4–12** with ZnCl₂ and with [ReCl(CO)₅] to give [ZnCl₂(**4–12**)] and [ReCl(CO)₅(**4–12**)], respectively, but neither was liquid crystalline.

A series of metal complexes was also prepared using the β -diketonate ligands as indicated in Fig. 1. Thus, a 2 : 1 complexes was obtained using Cu^{II} (**12**), which was found to be mesomorphic, melting to the nematic phase at 224.6 °C and then clearing at 241.3 °C. Complexation to oxovanadium(IV) was also productive and complex **13** melted at 130 °C to form a SmA phase, which gave way to a nematic phase at 176 °C. The nematic phase cleared at 240 °C and on cooling the mesomorphic sequence reversed, showing no evidence for decomposition. However, we were not able to obtain DSC data for this complex as no events showed up during the scan, despite clear evidence for the transitions from optical microscopy. This is an effect we have seen before, but methods we have used previously for overcoming it (*e.g.* using a pan as a lid in preparing the sample) were to no avail on this occasion.

Recalling iridium(I) carbonyl complexes reported by Trzaska and Swager,⁹ complexes **14** were prepared by reaction of ligand **11** with [Ir₂(μ -Cl)₂(COD)₂] under an atmosphere of CO. The products were orange in colour and showed the characteristic two carbonyl stretching vibrations in the infrared spectrum at 2069 and 1993 cm⁻¹. On heating, the complexes melted at 150 °C forming an isotropic liquid which, on cooling to 121 °C gave way

**Fig. 1** Structures of mesomorphic complexes of the new β -diketonates.

to a nematic phase, characterised by its schlieren and marbled textures. However, while the complex was pure by ¹H NMR spectroscopy and elemental analysis, insoluble impurities were observed suspended in the isotropic liquid on cooling. Further, when the material was heated for a second time, the original melting point could not be reproduced. Comparison of the clearing point of the apparently monotropic nematic phase with that of the two precursors to **11**, namely **8** and **10**, showed that *T*_{NI} was almost exactly the average of the two, implying that on heating/melting, the complex and its ligand decomposed to give the precursor methyl benzoate and acetophenone.

Finally, the palladium(II) complex **15** was prepared *via* the dinuclear *ortho*-metallated complex with bridging acetate ligands. As indicated above, complexes of this type¹⁰ normally derive their liquid crystallinity from the *ortho*-metallated imine, but in the present case the intention was to switch things around and to let mesomorphism be driven by the β -diketonate. This in fact turned out to be the case and so on heating **15** was found to melt to the isotropic phase at 202 °C which, on cooling, gave way to a nematic phase at 168 °C and then a SmA phase at 136 °C. Further cooling showed no evidence of crystallisation and so it is assumed that the complex forms a glass on cooling. Re-heating simply reproduced the SmA–N and N–I transitions showing that there was no decomposition.

Thus, employing a simple functionalisation of 2,2'-bipyridine and acetylacetone, ligands are obtained that can induce liquid crystal properties in a range of simple metal complexes.

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